Non-conventional Energy Resources
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Lecture – 36
Characterization of Electrochemical Devices

Hello in this class we will look at Characterization of Electrochemical Devices. Through this course we are discussing a range of electrochemical devices primarily because when you look at renewable energy technologies; invariably energy storage or you know generation of energy locally is a critical aspect of the big picture of you know renewable energy technologies.

So, even if you were to use solar power you typically have batteries associated with them or if you want to you know run clean with clean energy using hydrogen; then you would often have you know fuel cells associated with them and so, on.

So, invariably there are electrochemical devices in the background of you know which contribute dramatically to these overall success of the electrochemi of the renewable energy technology systems that are put in place. And therefore, there are a lot of companies that work or industries and companies that work on generating these devices, there’s a lot of research that goes on in various laboratories around the world to come up with better devices, to come up with more inexpensive devices more reliable devices that will help us you know in this requirement of our energy.

And so, electrochemical devices form a very critical aspect in this picture. And when you do work on these devices you need to do what is called characterization of the device by that I mean you have to understand that as the device is operating; what aspect of the what are first of all the various activities that are happening within that device that help you generate the current that you are happening to see that you are seeing on the external circuit.

So, something is going on inside the device, a set of steps are happening within the device that helps you generate this current. So, you need to know as a function of time or even as you know as a as a brand new unit that you get; how well are those various steps occurring right. So, you need to know how well those various steps are occurring and.

So, if for example, after some period of time the device is not functioning as well as it was on the day you purchased it, it is of interest to see which step has deteriorated maybe not everything has deteriorated maybe only something specific has deteriorated and therefore, it may be there may be some simple way to set it right, right.

So, many manufacturers and many scientists are keen on understanding the way in which electrochemical devices function. And to understand the way in which these electrochemical devices deteriorate as a function of either operating condition or time or a variety of other reasons and so, this process of trying to understand what is going on within that cell is referred to as the characterization.

So, characterization in this case we are doing characterization of an electrochemical device or a set of different types of electrochemical devices. And actually this is a very broad field I mean there are a lot of things that can be done to characterize electrochemical devices.

So, we are actually going to focus primarily on a few specific ways in which you can characterize electrochemical devices. And in this class we are really going to look at a couple of them which are the you know most significant ways in which we characterize these devices and are of or also of you know relatively easy approaches they represent relatively easier approaches of characterizing these devices and therefore, they are of interest and so, that’s what we will focus on in this class.

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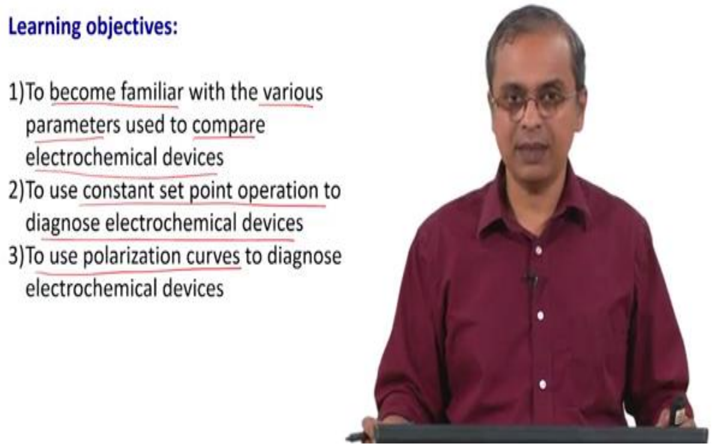

So, the learning objectives for this class are as follows we would like to become familiar to become familiar with various parameters that are used to compare electrochemical devices ok. So, what are these parameters that people use to compare electrochemical devices? What do these parameters represent ok. So, you may hear a term, but what does it really represent?

So, that's something that we need to get a better handle of; a better feel for. So, that when you hear those terms or hear numbers for those terms for various devices you have a better sense of what is it that they are referring to. So, we will look at; we will try to become familiar with the various parameters used to compare electrochemical devices.

And in that we will use actually two different ways in which we are looking at characterizing these devices. One is to use constant set point operation constant set point operation and using that you get a sense of what is going on in that device ok. So, that is one important starting point and in fact, often that is the starting point of any test. So, we will talk about those testing you know protocols. So, to speak as we proceed and that also helps us at least indicates when we need to diagnose it further; if it if it is not directly a diagnosis of something that's happening in the cell, it certainly gives you an indication of when we need to diagnose when we need to intervene and diagnose that cell ok.

And then we will also look at the use of something that is referred to as a polarization curve; polarization curve and it's a very important and useful way in which you can gather data from the cell. And using this data you can do some diagnosis of the electrochemical device. So, these are broadly our learning objectives; so, as we proceed with the class we will try to address this things. So, we will start by first trying to become familiar with various parameters that are being used to describe electrochemical devices.

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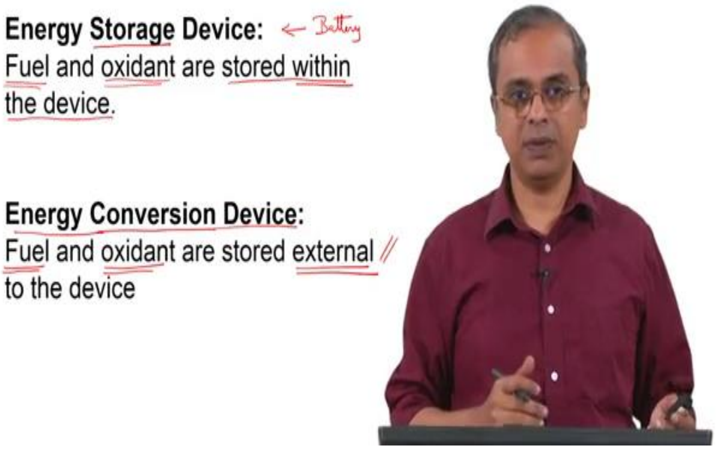

So, in this context I think it is of interest first of all to get a sense for these two terms here; one is the idea of an energy storage device and the other is the idea of an energy conversion device ok. So, the primary difference between these two is is related to where the reactants of are situated.

So, a typical energy storage device a good example of an energy storage device happens to be the good old battery that we use in a household applications batteries or cells that we use a common place you know in your remotes, in your mobile phones all those batteries and cells that we use are excellent examples of energy storage devices they are energy storage devices. And as you can see here in this description; it says fuel and oxidant are both stored within the device. So, fuel and oxidant are both stored within the device; so, in other words it means all of the reactants are stored within the device; physically stored within the device.

So, just keep that in mind and then we will discuss it a little more in in just a moment. As I mentioned the other kind of device is one which is referred to as the energy conversion device and here as opposed to the energy storage device the fuel and the oxidant are stored external; they are stored external to the device ok. So, in this case they are stored within the device, in this case in the in the energy storage device they are stored within the device, in the energy conversion device they are stored external to the device.

Now, at this level of description these two do not seem to be dramatically different. I mean it doesn’t seem like a big deal of a difference between these two definitions that I have given you, but operationally they are drastically different. And that’s the reason why it is of interest to first of all look at these devices and first figure out whether its an energy storage device or an energy conversion device.

So, what is the difference? So, as I mentioned in an energy storage device fuel as well as oxidant are stored within the device which basically means all the reactants are stored within the device; which again implies that the size of the device besides or is a good indicator of how long that device can operate. So, the size of the device is a good indication of how long the device can operate.

So, if everything else is the same in other words chemicals being used is the same, the current being drawn from the device is the same, the end use that it is being put for is the same then if you have a if you have a battery that is this big versus a battery that is very thin; then the big battery will last much much longer than the thin battery if everything else is the same. Let’s say it is it has twice as many chemicals as much chemicals; it will last twice as long ok.

So, therefore, a double A battery will last longer than a triple A battery for essentially the same application if you put it to use where you are drawing the same amount of current with everything else being the same. Assume it’s the same manufacturer and use using the they are using the same chemicals and they assembly assembling it in the same manner; if everything else is the same then the double A battery will last longer than the triple A battery. So, that’s the idea of the energy storage device.

Now, the energy storage device carries with it certain you know aspects of of itself which causes you know specific issues with respect to usage of those devices. So, as of now if any as we approach the year 2020; you see a lot of renewed interest in trying to put electric vehicles on the roads ok.

So, one common approach being used; one approach being used by a number of people who are interested in this process is to use electric vehicles based on batteries. So, lithium ion batteries are being used to power or different types of batteries maybe lead acid may be lithiun lithium ion, increasingly it is lithium ion that is being considered as the battery of choice to power an electric vehicle.

So, now given that all the reactants are stored within the scope of that battery; when you completely drain the battery, you have to either replace the battery which is one mode of operation or you have to recharge the battery right. So, there is a signica significant physical activity that is involved and so, if you have completed running you know say let's say 100 kilometers of operation, if that is the range of a vehicle. After operating the vehicle for 100 kilometers or maybe more maybe your range of operation is more than that in design for some longer operation.

And then let us say its 200 kilometers; you complete 200 kilometers of driving at which point you have to stop and recharge the battery and that could be a process that could take anywhere from you know 2 to 2 to 3 hours to maybe once 6 7 hours and in fact, generally all these batteries can hold more charge if you give them longer time to charge.

So in fact, the slower you charge the battery the longer it will hold charge ok. So, or it will take up more charge it will take up more charge and therefore, it will also hold the charge longer and therefore, the fuel energy storage device operates within those parameters that you have to now recharge the battery that is going to take several hours. Again then you will have a new fresh range of you know several 100 kilometers that you can run with it.

So, this is the scheme of operation alternately the manner of operation they use with these devices is they will go to someplace where they are completely replace the battery pack; they will give you a fresh battery pack and then you travel with that so that's one way.

The other option is to use an energy conversion device where the fuel and oxidant; fuel and oxidant are stored as I mentioned external to the device. So, this basically means the fuel and an oxidant are present in some tank. So, you have an oxygen tank or you are simply blowing air from the external atmosphere and you have fuel in some tank which is being piped into the device. And there the energy is being extracted from the fuel and then put some end use.

The nice thing about an energy conversion device is that you don't have to you don't have the process of a recharge so, to speak. So, when you are out of fuel you simply tank up again; it is just as just the same as what we do with your existing automobiles. In fact, the internal combustion engine which is present in most of the automobiles that we use these days is an energy conversion device.

So, the size of that engine whether it is a 1.2 liter engine or a 1.5 liter engine or a 2 liter engine; that size of that engine does not in any way indicate to you how long that engine will operate ok. So, technically speaking if you hadn't you know you know continuously you kept on changing the gasoline tank without a break or we kept on refilling the gasoline tank even when the without actually shutting down the engine which is at some far off location let us say you do that then technically you can have this engine running indefinitely right. So, so, you can consider a scheme of operation where this engine runs indefinitely simply by you know continuously running filling up the tank.

So; so, from the perspective of operation is dramatically different and the you know the complexity of those devices also varies a little bit due to these suttle differences between them.

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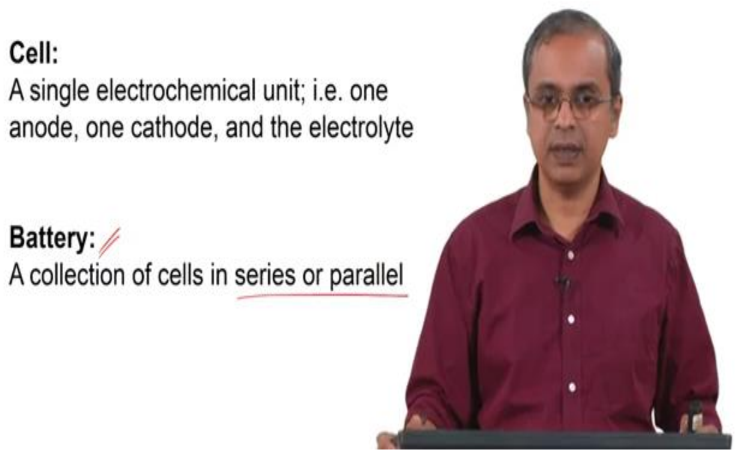

So, with this in mind we also should keep another definition in mind because these are things that we use as we discuss various devices. One is the idea of a cell and. In fact, often the single electrochemical unit that is there is technically referred to as a cell. So, when we say that we have purchased a double A battery or a triple A battery in a in a store actually what we are referring to is that we have purchased a double A cell or a triple A cell. If you put several of these in a in series or parallel then you have a created a battery.

So, if it takes several you know double A cells or triple A cells and then arrange them in series or parallel then you have a battery ok. So, that is just again something that we should keep in mind because we talk of these technologies; we should atleast be a little conscious of the terminology that goes with these technologies.

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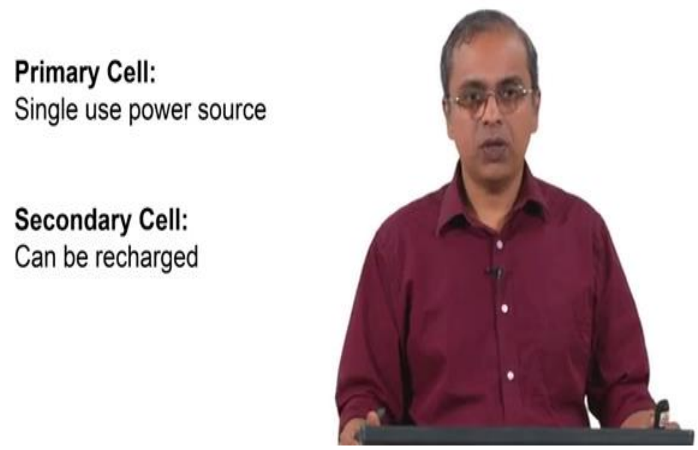

Also in this context we say you know a primary cell or a secondary cell and a primary cell is simply a single use power source. So, the batteries that are you know sort of use and throw away battery where it says do not recharge it will be written very clearly do not recharge; Because the chemistry in the battery such that it is not fit or it is not capable of being recharged. So, you simply use the battery and then you stop using the battery.

So, that's a single use battery; single use power source and the technical way of we refer to it is using this term as a primary cell A primary cell ok. So, that's the term that we use to refer to a single use power source. We can also have the secondary cell which is the cell that can be recharged and that is what we refer to as our rechargeable batteries as in our common usage common parlance we referred to a certain types of batteries as rechargeable batteries and that is basically a secondary cell.

So, these are some terms that I think are of interest that we should bear in mind as we do these kinds of discussion.

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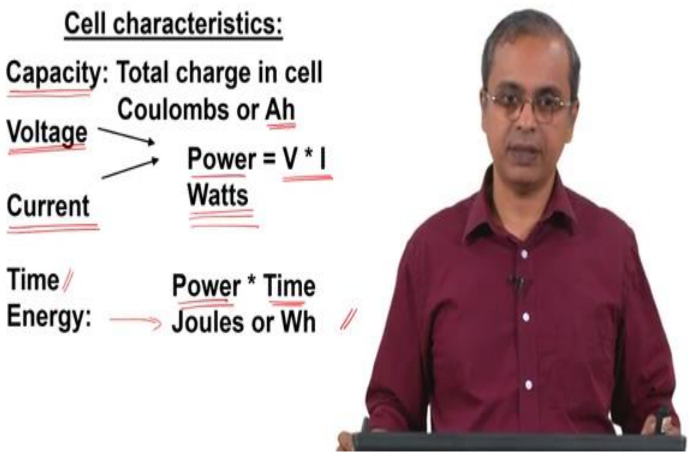

So, let's look at some cell characteristics here; the first is the capacity which is the total charge available in the cell ok. So, this is an indication of how long that cell can function. So, it is basically going to put so many coulombs that is available in it for to some use and in other words its it is measured in ampere hours. Amperes is coulombs per second and then you multiply it by a time in hours; so you convert into seconds and then you will get it in coulombs.

So, so this is the I mean terminology that is used and it refers to the capacity of the cell. Now as you can imagine for a energy conversion device; for a energy conversion device this is not really very relevant because you don't really have chemicals stored within it and therefore, in principle its capacity is unlimited. You can you know you can keep on putting you know fuel serving it fuel and it will keep generating energy.

So, this capacities of greater relevance when we talk of the battery. So, to speak the cells or batteries that we use which is the which is where the you know the chemical is within it and therefore, its capacity of is of relevance. Then we have two important terms here voltage and current ok. So, let's take a moment to keep in mind that you know you can draw a loose analogy of a voltage and current.

So, if you know look at an analogous situation of say you know water flowing through a pipe; then the pressure with which that water is flowing is analogous to the voltage that we are referring to here. So, voltage is sort of loosely analogous to the pressure of the water in the pipe and the amount of water that is flowing through the pipe is analogous to the current ok.

So, you can have high amount of current with you know; so, large amount of water flowing with low pressure, low amount of water flowing with high pressure high amount of water flowing with high pressure. So, you have all combinations right; so, four combinations you can think of low and high of voltage, low and high of current four combinations are possible right.

So, the same thing is yeah the way you would think of it with water; you can think of it with current and voltage and so, all these are possible. So, these are possible as a function of a brand new device itself a brand new device you take itself may be capable of high voltage, high current or low voltage, high current the kind of operation. So, you may have some combinations there; you may also have a situation where it starts off as a high voltage high current device, but in the course of its usage it becomes a low voltage low current devices things like that.

So, so, that is what we mean by saying there’s a performance characteristic that we have to understand; why is the high voltage high current device becoming a low voltage low current device after several hours of operation; so, this is something of interest to know. Power is simply voltage into current and we measure that as watts. And then we also have this idea of time that is involved as you draw this power from the system and therefore, we get energy which is simply the same watts that you see here times the multiplied by time.

So, power into time will give us energy which is joules or in watt hours. So, that is the other characteristic that is of interest; so, these are some characteristics that are of interest in the many of our electrochemical devices.

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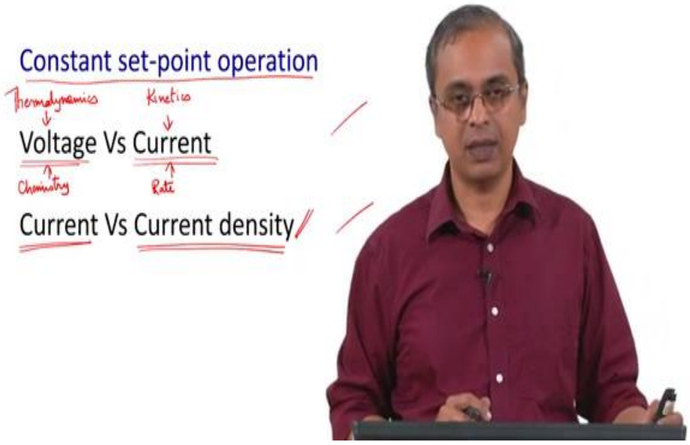

Now, I think it is very important to understand that you can have this idea of a constant set point operation; wherein you could either run it run the device at constant voltage or you can run the device at constant current. So, I think we should take a moment to better understand in the context of an electrochemical device; what does voltage represent, what does current represent? Ok I think it’s very valuable to have this thought process clear in our mind.

Because I think that relates to many fundamental things we see in so, many books and it relates to various calculations that are done and so, if you understand what is the difference between these two then you better understand why some calculations are used with respect to one and why some other calculations are used with respect to the other. So, voltage basically represents the chemistry of the system ok. So, you have some reaction occurring you have some reaction occurring at the anode, you have some reaction occurring at the cathode and as a result of what reaction is occurring ok. So, what is that constituent that is reacting, what is the product that is being generated ok? So, that choice of reactants and products decides the voltage ok. So, this is due to the chemistry involved chemistry ok.

So, what is that reactant and what is that product? That decides the voltage that is the chemistry involved. And therefore, this is of relevance from the perspective of thermodynamics ok. The thermodynamics of a system basically deals with what will happen under equilibrium conditions you will give it the best condition possible for the I mean you give enough time for some reaction to occur; what is that reaction that is going to occur, what is the you know urge for the reaction to occur, what is the driving force for the reaction to occur that driving force represents itself as a voltage ok.

So, thermodynamics which basically talks about what is possible; what is possible is thermodynamics. So, it predicts that you know given nature has certain tendencies; what is possible that prediction is thermodynamics and that relates to the chemistry that is involved which talks about which reactants are present and therefore, which products will it form. So, that is the voltage part of it.

The current on the other hand relates to the rate at which the reaction is occurring ok. You have independently decided what is the reaction that will occur? That is the thermodynamics of it; what is the reaction that will occur is decided by the thermodynamics that that is involved. The rate at which the reaction is occurring is the current; rate at which the reaction occurs is the current and therefore, this is referred to as kinetics ok.

So, the current represents the rate at which the reaction is occurring and in the in the field of you know science we are referring to we look at it from the perspective of kinetics of the reaction the voltage looks at what can possibly occur and in the field of science that falls under the realm of thermodynamics.

So, in some fundamental sense they have I mean you you can actually think of multiple situations where the two of them don't necessarily see eye to eye. So, you can have actually a good I main fairly high voltage, but you can also have extremely low current. So, which means there is a strong driving force for the reaction to occur. So, thermodynamics is saying that you know yes definitely this reaction can occur; there is strong reason why these two chemicals should react with each other and release energy.

But the circumstances in which that cell is situated are preventing the reaction from occurring at any appreciable rate; it is crawling along it is just crawling, crawling, crawling, crawling, crawling and therefore, the current that you are drawing from it is extremely slow okay. So, the point to remember here is in some ways the first starting point is the thermodynamics because supposing the reaction is not possible at all this thermodynamics says that this reaction is not possible. If it is not possible the chance that it will occur at any rate is anyway not there; so, it is basically going to be 0.

So, the kinetics is automatically going to be 0. Once on the other hand once the thermodynamics says that the reaction is possible, then we have a choice of kinetics you can select to you know either by your choice or simply because of the circumstances that are involved you can have a situation where the kinetics is slow or you can have a situation where the kinetics is fast. So, you can either have low current or high current.

So, voltage is one aspect of it; current is the other aspect of it and deals with the kinetics of it. From our from a user perspective all this is in the background ok. So, I say user when I go and buy a cell and I put it into a remote or I put it into a toy I am not concerned about you know what was the science involved in that you know deciding what chemicals are going to be involved there,, what is the you know is it set up to run naturally very well or it is set up to run naturally not. So, well those things are not relevant to me I want to draw good current I want it at a good voltage only then some devices working.

So, a scientist who is generating the cell bothers about these things; a user simply wants to know that it is delivering in a manner that is acceptable to him or her ok. So, that is the way we want to look at also we have this idea of current versus current density. In fact, as we discuss in this class I will focus more on current density rather than current and why is that ?

So, current in fact, is the inherent quantity that represents the rate at which the reaction is occurring, but we do recognize that you know you can buy if you are talking of a cell; you can buy a triple A cell or a double A cell or a D cell etcetera these are all of different sizes right.

So, they have a different differing amounts of chemicals present in them. So, I can have a small electrode of exactly the same set of chemicals or I can have a very large electrode with the same set of chemicals. Naturally if let’s say one electrode is half the size of the other electrode; naturally everything else being the same, the larger electrode can produce twice as much current as the smaller electrode because it has twice as much chemicals; twice as much opportunity to run the reactions etcetera.

So, every other condition being the same the larger; the electrode larger is its ability to generate current a larger the number of locations where the current the reactions can occur. Therefore, the rate at which overall rate of the reaction occurring over that entire area will be higher. So, therefore, it is not a fair comparison I can make with everything else being the same; same manufacturer, same chemicals, same packaging, same kind of packaging etcetera I can make batteries or cells of a wide range of sizes. I can make something you know as big as a room and there is no comparison between that and a small double A cell or a triple A cell that that may be there is no way of comparing.

So, it is important to normalize for the size of the electrode. So, you have to compare against a similarly sized electrode and the best way to do it is to look at current density there where we are talking of the number of amperes that can be delivered per centimeter square ok. So, once you talk of amperes per centimeter square; you have normalized with respect to area right. Once you have normalized with respect to area it doesn't matter how big the electrodes; however, big the electrodes you may have large amount of current, but you also have a large amount of area. Once you divide it the large current by the large area you will have the same value a small current by small area assuming everything else is the same.

Therefore once you look at current density; you have normalized for the area and therefore, the quantities become comparable ok. As I mentioned voltage simply talks of what reaction is going to occur and simply talks of what are the chemicals that are present. So, there whether it's a large electrode or a small electrode doesn't matter if only looks at what is that electrode is it a some particular reaction there is going to occur then that is going to be 1 voltage the size is irrelevant because its only doing that what is the electrode ok.

So, it is only looking at the quality or. So, to speak one characteristic of the chemical composition of the electrode it doesn't really care about the size of the electrode. So, by looking at composition it is sort of already doing a normalization because it is looking composition is some kind of a concentration that is already normalized in some sense. So, therefore, voltage is unaffected by size current is affected by size. So, current we need to look at as in the terms of current density.

So, in this discussion on this slide these are two important points that I wanted you to stay alert to one is voltage versus current the fact that voltage refers to thermodynamics or the chemistry of the system. And current refers to the kinetics or the rate at which some reaction is going to occur. And the fact that more than current it is current density that is of interest because that is when you can actually do a comparison between different devices ok.

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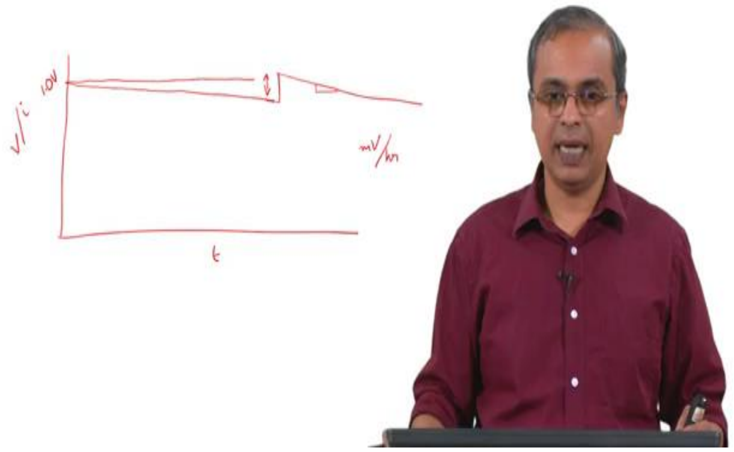

So, we now have you know as I said a constant set point operation which basically means you can have typically as a function of time. You usually look at voltage or current density which is you know often represented by small i and you see how that it functions as a function of time. So, let me say the opens open circuit voltage was 1 volt or the voltage under some operating condition happens to be 1 volt; then you would like to see how this voltage stays as a function of time.

So, so, for example, ideally you want it to just stay flat. So, you are drawing current for a long period of time and the voltage stays exactly the same value for this entire period of time. Usually this is not what you will see usually you will see that it steadily deteriorates. So, this is what you will typically see for almost any electrochemical device you tend to see this deterioration. So, this is a deterioration ok; so, deterioration of the functioning of the device.

So, if for example you are looking at if if we if if it were a battery for example, then you would actually run out of charge altogether; so, then that performance characteristic would look different. But let’s say it is an energy conversion device like a fuel cell then you would see your behavior that looks like this over a period of time then you have to find a way in which you can you need to recover this performance. So, sometimes there are ways schemes by which you can recover this performance and then again you let it run for a period of time and then it does this kind of thing. So, a lot of diagnosis is done using this to a first of all people look at degradation rates. So, they look at the slope of this curve at of this line here and that represents a degradation rate.

So, we talk of it in terms of you know millivolts per hour; degradation rate millivolts per hour degradation rate is something that people try to actively keep track of for many electrochemical devices. And so, they will have a target; so, if you are looking at any device you know other people who have looked at the device in a more holistic sense will set a target saying that you know if you have a device we want a degradation rate that is less than so, many millivolts per hour. So, it means it is degrading at a much slower rate.

So, that is something that we want to accomplish and that is the parameter that we want to keep track off as they characterize these devices. It also turns out that this rate of degradation the slope that I have just shown you on the on this slide can actually vary significantly with time. So, in other words you may have a very gentle slope in the first say say 500 hours of operation and then you may have a much steeper slope from 500 to 800 hours of operation and it may just precipitously drop off after 800 hours of operation.

So, this is not even a constant slope. So, a lot of research is done to understand what is causing that slope to be a certain value for the first 500 hours, what is causing the slope to change between 500 and 800 hours and what is causing the slope to completely collapse after 800 hours of operation?. So, that’s just to give you some idea of you know the kind of work that is done; you can do this at constant voltage or at constant current correspondingly the other parameter gets measured and then you see that as a function of time ok.

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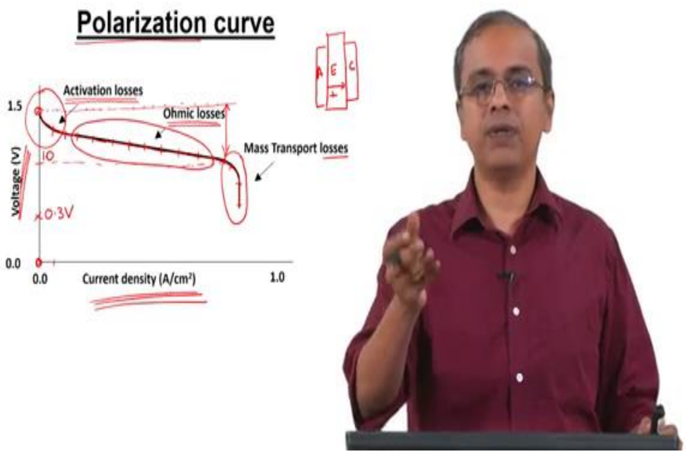

The other parameter that you looked at a lot is the polarization curve ok. So, polarization curve is a very important diagnostic tool where basically what we do is; as supposed to the constant set point operation where you are looking at you know operation of that device over maybe several hundreds of hours maybe several thousands of hours or if it is a battery you are looking at operation over several cycles several hundreds of cycles ok. So, that's it's a long you know process during which you find out what are the degradation rates and then you figure out what you can do to recover.

This on the other hand the polarization curve on the other hand is relatively instantaneous okay relatively instantaneous; meaning it's not actually totally instantaneous it takes maybe a few minutes to acquire this data, but it gives you a sense of the health of your electrochemical device at that instant in time okay. So, what do we see here? So, it is something where you are first of all not at one operating point you are steadily changing the operating point in a small span of in a in a span of several minutes okay.

So, you will have an open circuit voltage which means you can see here we have current density plotted here. As I said you know this normalizes for the area of the cell and you have voltage plotted here on the y axis. So, when you have 0 current in the system which is this point out here then you have some open circuit voltage which is that point that you see over there ok.

So, that is the open circuit voltage which if you know go by the device and you just put a voltmeter on either side of the device and you measure the voltage that's the voltage you will see then you start drawing current. So, this device now has to be attached to some you know unit which can draw current in a predictable manner. I should be able to say draw 0.05 amps per centimeter square that is the current density I want. So, it will draw 0.05 amps per square centimeter and then at that point it will tell me what is the voltage. So, let's say that is somewhere here then I will see this voltage ok.

So, so, gradually I will increase the current density; I will go to various points out here and I will keep measuring and in at at each condition I know exactly what current density I am using and for that corresponding current density it is measuring the voltage. So, it is measuring the voltages along the y axis for each of those current density values that I have just marked out there.

So, when I; so, this is a process that I said you know it will happen over just a few minutes. So, it will what the instrument will do is; it will take this device it will set the current density to be 0.01 or 0.1 amp per square centimeter it will measure the voltage it will stay at this point for let's say 10 seconds or 5 seconds; measure the voltage then it will go to 0.2 amps per square centimeter. Again sit there for 5 seconds, measure the voltage record those two go to 0.3; sit there for 5 seconds, measure the voltage record the voltage and so, on.

So, this process continues till you suddenly see that the voltage begins to drop precipitously right and so, you can set some cutoff saying you know if the voltage drops in this case that is set at 1.5 volts let's say I just give some value here let me say this is 0.3 volts. So, I will set some cutoff voltage say you know if you reached 0.3 volts stop the stop the curve and we reverse the direction of the current this gradually start decreasing the current.

So, invariably you will see a curve of the nature that you see on your screen here; it starts off at a high value out here of a voltage and then it starts sliding down. And then you see this curve that that is generated here it just goes down and then it precipitously begins to drop down. So, this is a polarization curve ok; so, that's a polarization curve.

So, now we want to understand what does this convey to us about the cell ok. So, it is a very useful technique because it conveys several interesting things about the cell to us;

the first thing is different regions of this curve correspond to different aspects associated with the cell. So, what you see in the initial part of this curve here relates to the; manner in which the reaction is occurring at the reaction site ok.

So, you have some reaction occurring at various reaction sites maybe there are catalyst sites that are present, maybe that there are anode materials that are present, cathode materials are present there is the reaction that is occurring at the reaction site right. So, at the reaction site whatever reaction is occurring; whatever difficulty it is facing in completing the reaction that is what is conveyed in this initial part of the curve.

Then in all electrochemical devices as as we have seen before you have an anode, a cathode and an electrolyte anode cathode and electrolyte so, in all electrochemical devices you basically have some ion; some ion that goes. So, some you know let's say a positive ion a positive ion is being transferred through the electrolyte. So, some ion is being transferred it doesn't have to be positive ion; I am just you know putting a positively charged ion get being transferred. So, let's say it is a proton; so, H plus I have just to just for something that you can keep in mind some ion is being transferred.

So, there is a conductivity associated with that transfer process usually that is the lowest of the conductivities that is there in that circuit ok. So, that conductivity impacts the slope associated with this region of the curve. And that is why this region of the curve is referred to as an ohmic loss okay this early part of the region is referred to as an activation loss; refers to the ease or difficulty with which a reaction can occur at the reaction site; this ohmic loss represents the ease or difficulty with which the ion can be transferred through the circuit through the circuit.

And finally, we have concentration losses or mass transport losses this represents the difficulty with which the reaction sorry the reactant is being brought to the reaction site ok. The difficulty or ease or difficulty with which the reactant is being brought to the reaction site which means what; So, for example, if you were in a few if you are considering a fuel cell the gases that you supply hydrogen and oxygen that you supply have to find their way to the reaction site right. So, they have to go through some force to arrive at the reaction site.

Now, you can have a situation where the you know where there is let's say water being generated and blocking the excess of the gas to the electrode; then this mass transport becomes bad. So, in other words it is unable to get enough hydrogen and oxygen to the reaction site and therefore, this drop off that you see will actually occur under much poorer conditions ok. And what are poorer conditions? Those are all what are listed here in your you know x axis and y axis.

Basically if everything were ideal; you will be able to draw a current at this open circuit voltage itself; if everything were you know beautifully ideal world that you have then you will get a considerable current at open circuit voltage. You keep on drawing higher and higher current voltage of the cell will not draw; it will stay some standard fixed value.

Real world nothing happens that way; as you draw current you are trying to make that reaction happen faster and faster and faster. When it tries to happen faster and faster it happens inefficiently these three parameters that I showed you the activation loss, the ohmic loss and the mass transport loss or concentration loss are inefficiencies that are present in the system because the reaction is struggling some energy is wasted there.

So, that is your activation loss because the transport of ion is struggling because you are trying to drive it faster and faster and faster; some energy is lost in the process in trying to drive the ion to get across the membrane. So, that is a loss that is an ohmic loss some energy is lost in trying to push this ion along and it is it happens to be struggling.

For some reason; the gas is struggling to reach the reaction site again your you know you know driving it too hard for the process and therefore, some energy is lost in the process. So, therefore, that is that is the reason these are referred to as losses in electrochemical terms they are referred to as polarization. So, polarization is a loss; so, this wherever I talk of a loss and I use this term polarization they mean the same. So, in based on the book you look at; it we will talk of activation polarization, ohmic polarization and concentration polarization here I am referring to it as a loss they are basically the same the same idea is being used.

So, ideally you should not have any loss; you should just have this nice flat you know profile for voltage and you should be able to get you know indefinitely get current at high voltage that is not what is happening, you are losing all this voltage. So, whereas, your battery was you know capable of giving you 1.5 volts, you put the you know volt meter across it and it showed 1.5 volts. When you start drawing current, you actually find that it is giving a much lower voltage which corresponds to this value here line here; if I just draw this line here. So, here for example, let’s say in this scale that I have drawn here this may be about 1 volt.

So, as opposed to be 1.5 volts that the battery was capable of giving when you draw current from it and at some appreciable level; it is actually only giving you 1 volt right. So, this is the loss and this is energy that has been lost from the system. So, you are only getting about two thirds energy that it is capable of giving you it’s not give giving you the full energy.

So,. So, this is a specific degradation of the system as a function of just the operating condition; it is got nothing to do with the; so, if you relaxed the operating condition you can actually operate the device with less losses. But this is a very very nice way of characterizing your cell because first of all it takes only a very small amount of time to do this characterization. And at the same time it is giving you information about three different processes that are happening in your system, you have activation process, you have ohmic process and a concentration process. So, all three processes it is trying to give you good information.

So, for example, if you compare two different cells or the same cell under two different conditions after two different operating conditions.

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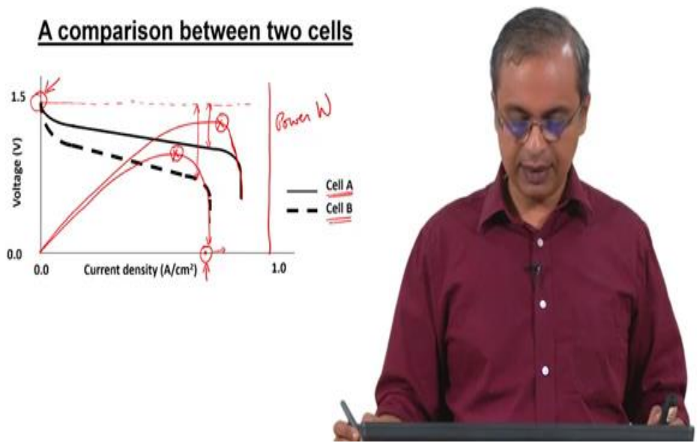

You may have something like this; we will look at this briefly let's say there are two different cells cell A and cell B; you can see here that these two have two different polarization curves ok. Let's just assume that these are two brand new cells ok. So, if you go to the shop; if you go to a store and you go and try to purchase a double A battery you can see that you know it will say 1.2 volts or something like that, but let's say it say says 1.5 volts.

So, you take a brand new battery from our brand new cell from one manufacturer, you put a voltmeter across it shows you 1.5 volts. You take a brand new cell from another manufacturer and you put a voltmeter across it; it also shows you 1.5 volts. So, both of them coincide at this point.

Now, you take these two cells and you put them to a test ok. So, every manufacturer say you know my cell is better than the other person cell right; they all say that everybody advertise they say my cell is so, much better than the other person cell, you should buy it kind of thing. How do you know that it is better or not? This is the kind of test you do you take that cell and you put it through a polarization curve ok. So, you can see here for example, cell A as I as I said in ideal condition you should see no drop in voltage that is idea. In fact, that is never going to happen; so, this is just for you know frame of reference.

So, what is actually going to happen is there is going to be some loss of performance as you draw current from it, but you want to minimize that loss that's really all it is. So, in other words this gap between this ideal performance and this actual performance; you want to minimize that gap because that gap represents loss. So, you want to minimize it; so, you want a polarization curve that looks closer and closer to the ideal curve right.

So, in other words this cell this second cell that you see a cell B has a much more significant loss compared to cell A right. So, if you actually were trying to draw some significant amount of current from cell B you will find that when we once you reach this point for example; it is unable to actually deliver any higher current than that.

If we try drawing any further current from it the voltage completely drops precipitously drops; the voltage precipitously drops. And once and voltage represents the driving force if you don't have voltage; nothing is going to go through your circuit and then basically it comes to once you have 0 voltage it means there is no further driving force for any current to go through your circuit, nothing is going to happen; it’s all going to come to a halt.

So, clearly for any current density higher than this operating point this operating point that I am marking here; you cannot use cell B you can only use cell A right. This is despite the fact that at the starting point; they both look exactly the same right. So, when you purchase this from a store it looks like you have got two cells of identical you know capabilities, but when you actually put them to use; they are actually dramatically different they are not in a position to perform anywhere close to each other.

So, this is I will come back to this in just a moment. So, as I said you know the voltage times current is the power.

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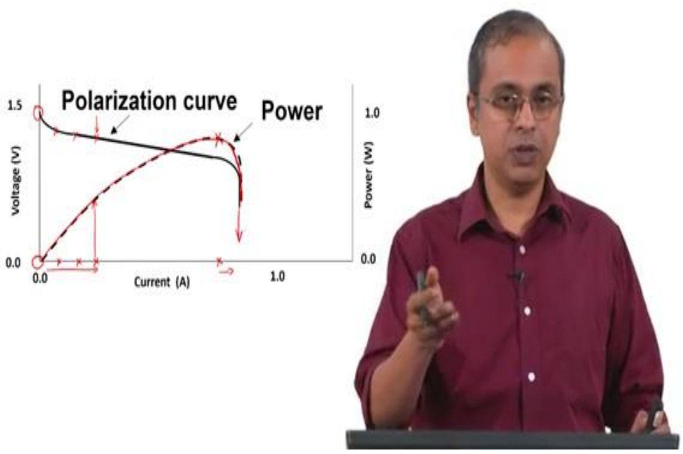

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And so, that is actually shown to you in this curve here, where we are taking the polarization curve and also adding the power curve corresponding to it. It means so, for example, if you see here you have high voltage 1.5 volts right that’s the open circuit voltage at that instant in time you are actually drawing 0 current.

So, the power you are drawing from the cell is 0; 0 watts you are drawing ok. So, 0 0 watts I have put current here you can put current density also here; so, its 0 watts. So, as you start drawing more and more current, as you go up I mean along this axis; correspondingly the voltage is coming down. So, if you take the product, but the voltage is coming down gradually; the current is going up fairly significantly it’s it is only a gradual drop here, but the current has actually gone up this much. So, you have a fair bit of power; so, power is actually going up.

So, power keeps increasing along this line power is continuously going up. So, this continues this process continues; so, you see this continuous increase in power, then you reach a point where you have now reached a value of current where if you cross this value of current the voltage is beginning to drop precipitously. Because the voltage drops precipitously the overall power is also dropping precipitously. So, the power begins to drop precipitously right.

So, therefore, this represents the maximum power that this you know electrical chemical device can deliver; this represents the maximum power that this electrochemical device can be deliver. So, if you are actually doing a project and you really know what you are doing; you are doing a project you have some some number of devices that need to be powered by a power source.

You need to figure out how much power those devices require right; you need to understand what is that power that is required by those devices that are now in your circuit and that total power that it that is required when you buy a power source for that device for that circuit that you have created that power source should have a maximum power that is distinctly higher than that maximum power that you are going to draw.

If on the other hand, the maximum power that the power source can give is less than the maximum power that your device can is requiring; your device will not function it will or it will at least not function as well as you want it to function, it will just struggle it will struggle maybe parts of it will work parts of it will not work or it will completely not work it will basically either work sluggishly or completely not work.

So, you may think that you know because of the components that you have got; it will actually function very well, but because the power source that you have selected is such that you know its power maximum power is less it is not in a position to actually support this end use that you are putting into.

So in fact, if we go back here you can see again in these two cells that you have here the two the maximum power point that you can get from these two cells will also be very different. So, if I plot a power on this and had a power axis also on the y axis; then let's say I put power here in watts, then you will see that the corresponding to that you will have for one; one cell you will have a curve that looks like this. And for the other, you will have a curve that looks like that something like that; so, this is a schematic. So, clearly you can see that you know this is a much higher maximum power that it is delivering to you; this is a much lower maximum power that it is delivering to you.

So, clearly for whatever end use you are putting to you know; cell A is a much better position to deal with that end use than cell B right. So, the this is how these two cells compare; so, if you look at our polarization curve and you see a few different ways in which the system might have deteriorated with time. So, we will see them show up in certain interesting ways with respect to the polarization curve. So, first let me just draw here the polarization curve schematic of a polarization curve that looks okay.

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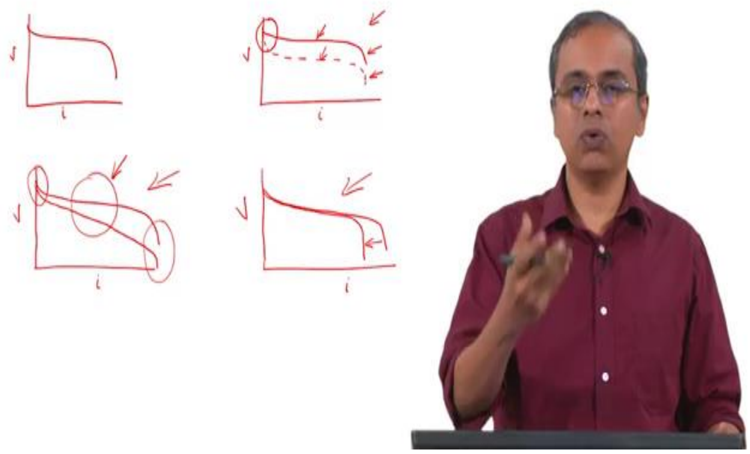

So, we have V and we have i and you see a curve that looks like this right.

So, now if for example, after some hours of operation; the let's say the catalyst or the reaction site has alone become bad and everything else is fine with that cell, then you will see a polarization curve that will change to something like this. So, I will still draw the original one here and then we will look at how that is changed. So, we will assume that this is the original one that has done something like this; you will now see the new polarization curve that looks like this.

This means the activation energy losses alone have gone up in a very dramatic manner. On the other hand the ohmic losses as well as the concentration losses are roughly the same. So, it means that they are not affected and so, this is a very nice way in which you are able to isolate the region where you are having the deterioration occurring in the cell.

Similarly, if we would also look at the two other cases where let's say only the ohmic process has gone bad or only the concentration processes is deteriorated. So, you will correspondingly see situations that look like this let's say only the ohmic loss has become worse. So, you have V and you have i here current density again the original curve looks something like that. And now let's say only the ohmic loss has become bad; so, you will now see the original activation system looking like that. And then you will see this huge difference in the slope and drop off like that.

So, the main difference between these two curves is the slope in this region whereas, this region is largely unaffected, this region also seems to be largely unaffected. So, this is the region that is affected and this implies that only the ohmic losses have become worse in the cell whereas, the activation losses as far as the concentration losses are roughly the same as before ok. So, we have now isolated the component where the problem is and therefore, presumably you can you know do some appropriate improvement on the component.

The third possibility as you may guess would look something like this is the voltage, this is the current density, again this is your original curve. And then you have everything else being the same only the mass transport losses have become bad and that would look something like this to retrace the path, but this alone will drop down.

So, in other words only the concentration losses now become worse. So, so we now see that you know using just the polarization curve; you can have three situations. In one case the reaction site has become bad the; in other case the that would be this example here the other case would be one where let's say the membrane conductivity or the electrolyte conductivity has become bad and that could be this situation out here.

And the third would be one where some you know pathway; some pathway for the reactants appearing at the reaction site is getting blocked. For various reasons, it could be that some old reaction product is you know has formed some irreversible reaction is just blocked some you know has left some precipitate which is blocking the path for this reactants etcetera and therefore, the pathway for the reactants has been blocked.

So, this is a very nice and simple technique where you are actually going to run the cell at specific operating points from just a few minutes. And in that process you are going to be able to compare and figure out which component has deteriorated; this deterioration could have occurred as a function of time or this deterioration could simply be a you know artifact of how use happened to make that particular sample. And therefore, it gives you some insight into how you can go about improving either your process or your product.

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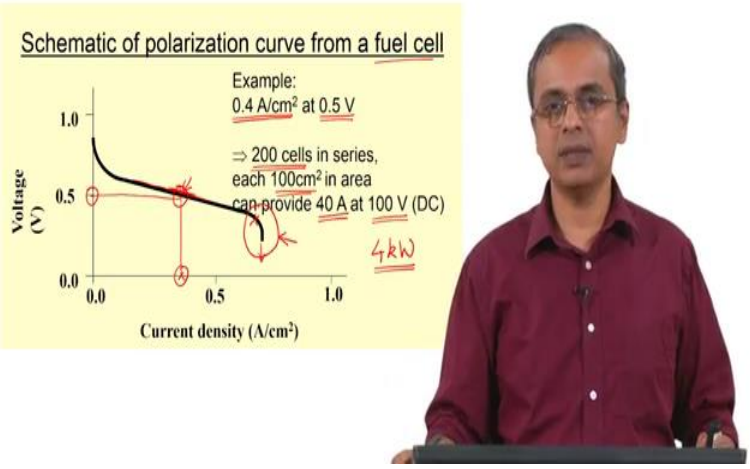

So, for example, you can see here you know I mean how this is useful in a in a in the broader sense of the usage of electrochemical devices. And that you can see with an example of a polarization curve from a fuel cell you have you know it let’s say it is this is what is possible with the fuel cell; this polarization is what is curve is what is possible from the fuel cell. So, this is how we use the polarization curve to decide what you can do with that electrochemical device right.

So, you run this test independently, you get this polarization curve available with you and you have it available to you and then based on that you make a decision. So, for example, let’s say I have this device and it has shown me this polarization curve it is all normalized I have voltage on the y axis I have current density on the x axis.

So, I choose an operating point of 0.4 amps per square centimeter that's puts me somewhere here. And then I look at what voltage it will give me. So, that gives me a voltage roughly about 0.5 volts ok; so, that's what voltage it is going to give me. So, that's the operating point for 0.4 amps per square centimeter and at that point these electrochemical devices in a position to give me 0.5 volts.

So, ok; so, this is this is how I use the polarization curve to first of all figure out what I can expect from the device right. So, if now I have 200 cells in series and let's say each cell has a area of 100 centimeter square; then because it is hundreds centimeter square and you have 0.4 amps per square centimeter as the current density, the current corresponding to it is 40 amperes this represents the rate at which the reaction is happening.

So, at 40 amperes that many I mean amount of that much amount of chemicals is being consumed is the corresponding amount of chemicals is being consumed to create that number of electrons in the circuit which will correspond to 40 amperes ok. So, a coulomb per second is an amp; so, you have you know 40 coulombs per second that is being generated. And then you can correspondingly calculate the number of electrons required for it using 1.6 into 10 power minus 19 coulombs per electron as the charge.

So, you know how many electrons is required and then based on the chemistry you can decide how many moles of you know whatever reactant is being consumed because each model generates some number of electrons some number of moles of electrons.

So, now we also said that you know I am I have put together a you know battery where you have 200 cells in series and those 200 cells are all each of them is operating at 0.5 volt. Therefore, the total voltage of that unit is going to be 100 volts. So, between 40 amps and 100 volts I have 4 kilowatts; 4 kilowatts of power that is being generated from this unit. And this is the polarization curve corresponding to this unit and therefore, I mean I am able to set this point with as this as the set point for this unit with good confidence that you know I am operating at a relatively a to the safe area.

So, please note that you know right here I am sort of in the middle of this polarization curve here. So, I am in a fairly safe you know operating point as opposed to being down here; where I am at a you know shaky operating point meaning by that I mean you know if the operating point changes marginally; I am not going to see a collapse of the system.

If I am here if I am already operating at this you know knee knee of this curve; a slight variation in the operating point will see a precipitous drop in the voltage obtained from that device. Whereas, here a slight changes in the operating point will simply have me sliding fractionally up and down this region here right; it doesn't lead to a precipitous drop in the operating point of that system right.

So, so, these are the things that I wanted to discuss with you today we have looked at you know constant set point operation and how it shows you that something is deteriorating, how you can look at that to see if it started deteriorating more or deteriorating less. And then you know use that to set some kind of a set point on what deterioration you will tolerate.

We have also looked at polarization curve and how it is able to show us three different parameters in the cell; things that are you know related to the reaction, things that are related to the transport of ions in the system and you know losses associated with the concentration you know issues associated with the system.

So, these are you know ways in which we characterize the cell. A very useful information we get from the cell; there are many more techniques and even more interesting ways in which we can look at you know even the polarization curve which we can look at in greater detail at some other point. But this is a very good overview of what can be done with the polarization curve and what are some of the; key parameters that it conveys to you.

Thank you.

KEYWORDS:

Characterization of Electrochemical Devices; Constant Set Point Operation; Fuel Cell Testing Protocol; Polarization Curve; Energy Storage Device; Energy Conversion Device; Cell; Battery; Primary Cell; Secondary Cell; Single use Battery; Cell Capacity; Parameters of interest in Electrochemical Device; Voltage; Current; Kinetics; Current Density; Activation Polarization; Ohmic Polarization; Mass Transport Polarization; Concentration Polarization; Power

LECTURE:

This discussion gives a detailed idea on how to characterize electrochemical devices by using single operating point mode and generating polarization curves. The polarization curve, its shape and the meaning of slope of such a curve at different regions of the curve is connected back to the loss in voltage due to some process or a particular part in the electrochemical device.