

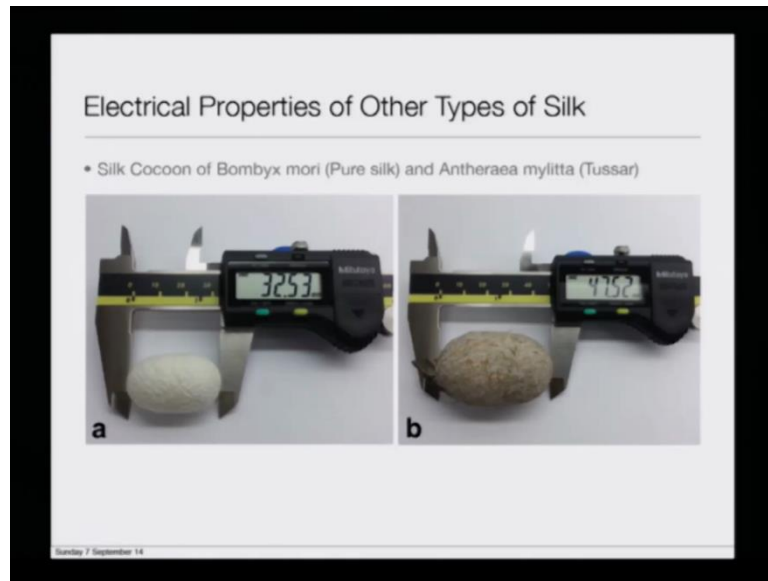
Bioelectricity
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Lecture – 40

So, let us start the fortieth lecture today which is on silk biomaterial, and electricity. So, in the previous lecture I shared the story of Jacob Ishay, and his exploration of understanding the thermo photovoltaic properties of hornet silk cocoon membrane, and which is also called the silk cap. So, today will be talking about the other cocoon membranes which is the more traditional ones the Bombyx Mori, and the Tussar cocoon likewise, and we will see whether the observations which were made by Jacobmisrsigen during nineteen seventies eighties, and nineties with the seminal word do they really hold true for more commonly known silk or is it just a very unique property of the hornet nest as I told you in previous lecture that in one of the studies, it was observed that the regular silk cocoon has a thermoregulatory property that gives a positive hunch that possibly if it has a thermoregulatory property it may have certain currents across its membrane. So, this lecture will be to explore that, and further whether these kind of hairy currents.

So, you know very small current could these currents may be utilized in the era, when we are kind of you know facing lot of energy crises as we are looking for different kind of materials to generate power could. These kind of naturally existing material could be utilized you know power some low power electronic devices or not. So, this study will take us from ashes original study on hornet nest to the next level of study, where we will be dealing with the silk cocoon membranes of Bombex, and antheraea mylitta. So, this is the repetition of the picture what I showed you people.

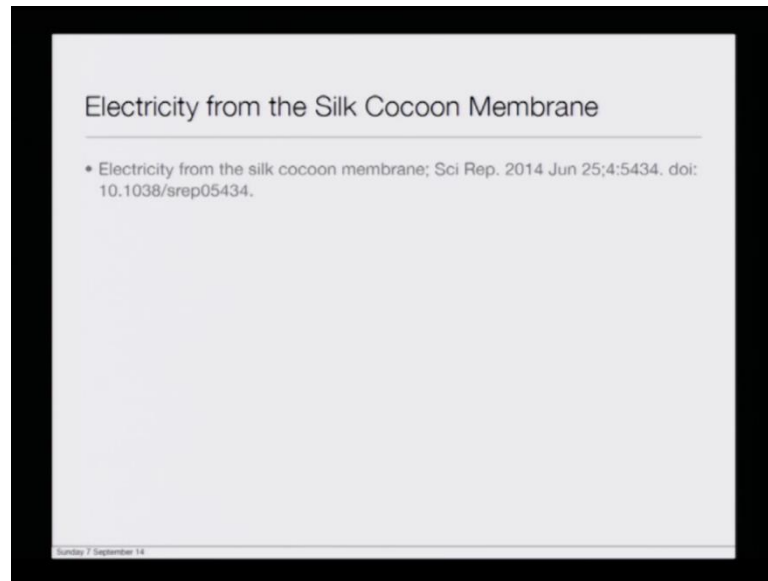
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So, if you look at these two cocoons. So, on your left hand side with a is a Bombyx cocoon. Bombyx is the most commonly used cocoon for the garments across the world. China being the largest producer followed by India, and this cocoon is very smooth. Cocoon, and very this silk is very smooth, and it does not have a lot of minerals. It is very very little mineral contents, and that is why it is so smooth and so fine. Where is the second one on the b what you see a Antheraea mylitta or a Tussar cocoon. This is also called a wild cocoon, because it grows in the wild or some time very domesticated, but kind of you know.

So, this cocoon has a lot of mineral contents, and that is a challenge in order for a reeling labor, because of the lot of mineral contents this cocoon has a kind, of course it has a very coarse texture as compared to the texture of the Bombyx mori cocoon. So, in this lecture we will be talking about the electrical properties of these two types of cocoons.

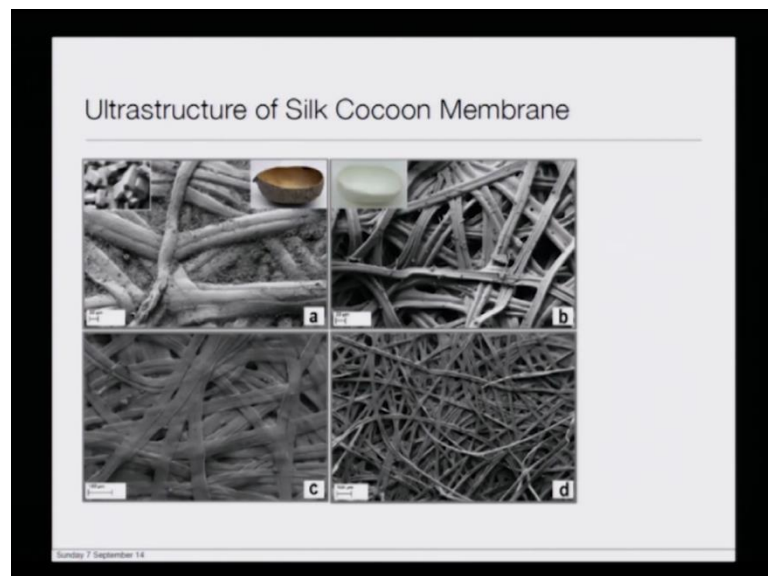
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So, let us talk about the ultra structure of these cocoons. So, this is the paper I will be referring to. So, I will be adding this paper in your additional material reading material please go through this paper. So, all the studies what is being shown is will be from this paper and.

So, that sums of there are three papers what I expect you from the previous lecture those two papers from jacobishay, and this paper from scientific reports please go through them, let us move on to the next lecture .

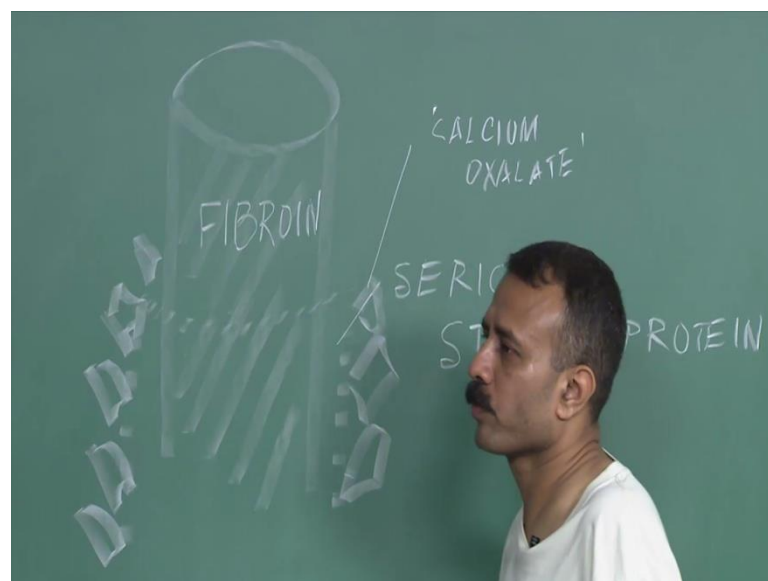
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So, if you look at the ultra structure of the silk cocoon membrane on what you see on a is the ultra structure of the anthereaea mylatter or tussar silk, and b what you see is the ultra structure of the bombyx mori cocoon, and if you look at the structure very carefully you will observe a, and b the basic difference is a has lot of in you know as if the granules granules scattered on the sericin fibroin network where as you see a very smooth texture in the case of bombyx.

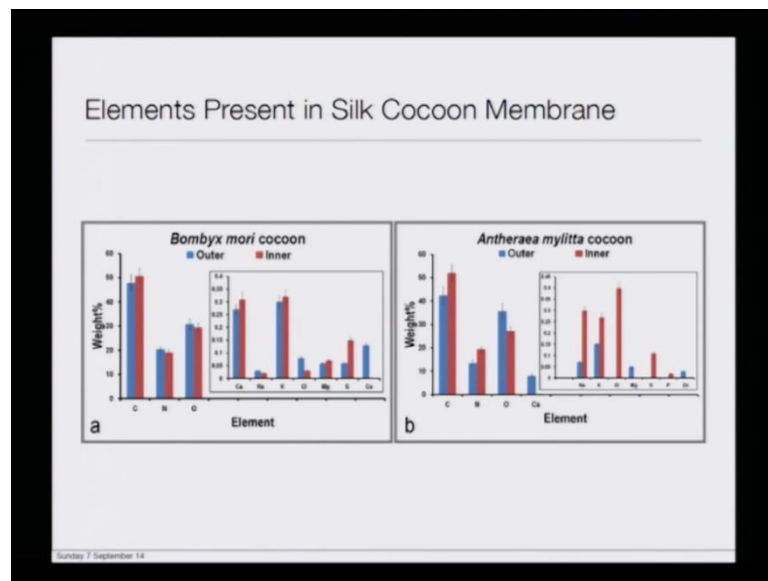
Now, the upper two panels are showing the outer surface of the silk cocoon if you see the inner, because it has been cut into into two halves. So, that what you see is the outer surface, and what you see here is the inner surface both inner, and the outer. So, the lower two c, and d are the pictures of the inner surface which is fairly smooth in both the cases, but in terms of the fiber thickness the fiber is quitely more thicker in the case of the anthereaea type of cocoon or which is also called as tussar cocoon, and a, and b which is the outer surface of the cocoon what is being shown see the threads are coarse coarse as well as the case of anthereaea. And you see there is a inset box which is showing some you know in the left hand top corner, if you see it those are seeing the crystals what you see those small small you the granules all over the surface it is showing the crystals of calcium oxalate they have enormous deposition of calcium oxalate on their outer surface.

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So, this is the basic ultra structure, and the basic ultra structure still follows the same way what I showed you the inner cylinder inner core cylinder of fibroin, this is the fibroin core, and this is the gummy part which is the sericin or the sticky protein, and on top of the anthereaea mylatter what you see you see lot of sticky crystals which are present here. And these sticky crystals are of calcium oxalate what you see in the inset picture. So, the basic geometry is the same there is no difference in the basic geometry except there is one more change what you will observe in the next slide is this one.

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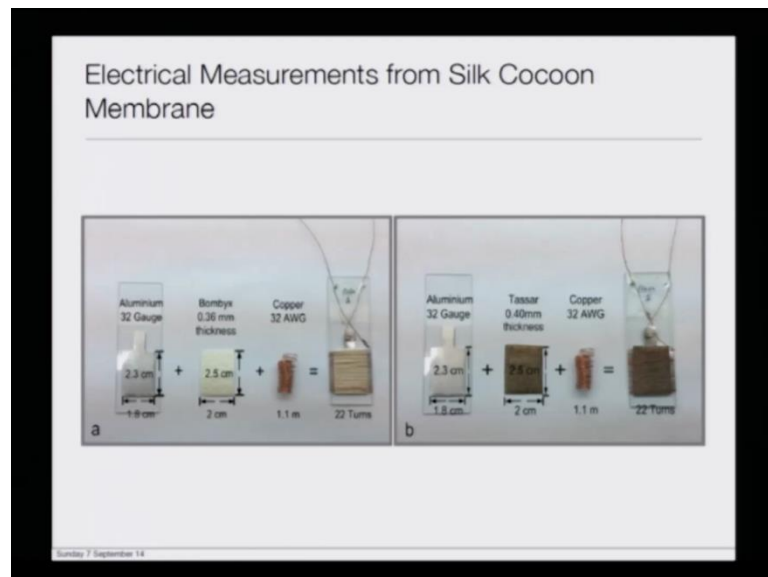
The amount of elements which are present in it this was also observed by jacobishe while talking about the silk of the hornet nest. So, if you look at it there is significant proportion of calcium sodium potassium chloride magnesium sulfur, and copper, and where as in the anthereaea you pretty much see the same except they have zinc, which is insignificantly higher amount at least not detectable in bombyx, and their phosphorous which is not detectable in bombyx.

Of course the sulfur, and all those things are present, and the copper which is not detected in the case of anthereaea if you look at it there are plethora of calcium is higher in one of them which is in the anthereaea calcium is fairly higher, and that calcium possibly is coming from the calcium oxalate crystals, because there are there in in the anthereaea there is enormous calcium oxalate crystals, and that is why the concentration

of calcium is very high in case of antheraea mylatter. Now if you look at this. So, it means we are talking about I am adding one more component to it.

So, they have lot of these x are showing the different kind of elements which are present there, and one more thing here I want to add all the studies made by Ishay was when you are keeping the cocoon at a slightly higher relative humidity at around eighty percent relative humidity eighty percent to ninety percent humidity you are observing all the different currents which are observed by Ishey, it means the ambient water plays some critical role in charge transfer.

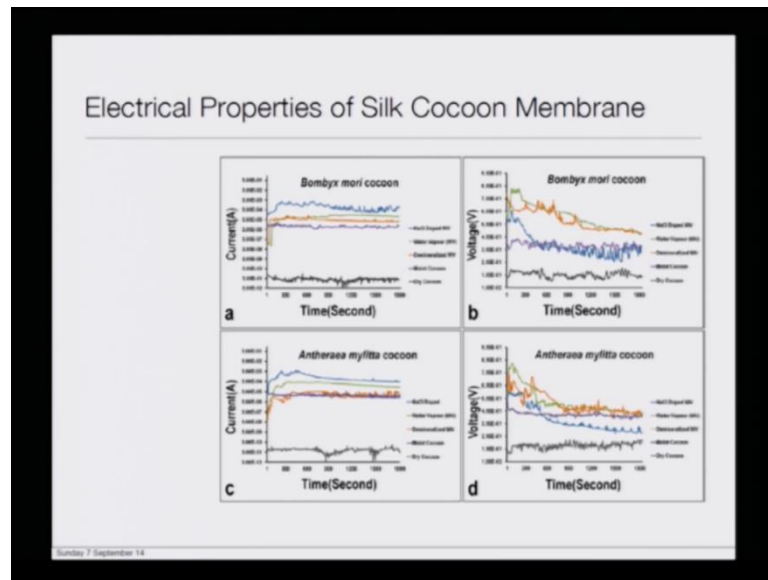
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So, now moving on to the next slide in order to understand how the cocoon properties could be studied you have to develop certain very specific standard structure. So, what has been done in this study is you took two different cocoon samples took a piece of bombyx, and the measurements are given out here they have a slightly varying thickness that you cannot help it, because there is inherent property, and you connect it to two different electrodes. So, here let me add they have a certain amount of voltage across the cocoon across the membrane, but that voltage is not very high as was observed by ishay. So, in order to enhance that. So, silk cocoon has its inherent potential difference p d one which is indigenous potential difference, and now by putting two different electrodes say an aluminum, and copper you are adding one more potential difference to that which is the second one.

So, the total potential difference is now slightly higher. So, now what you are using is in order to understand, because we are more keen here to see whether this could be used to you know develop some kind of device or not we know that there is some low current, and all those things, but could this be utilized

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So, the next study what has been done by developing these kind of devices the current, and voltage are been measured, and now let us see how the current, and voltages are changing. So, if you now see a dry cocoon now follow this is a busy busy slide go to the panel a. So, see in the panel a in the case of a dry cocoon there is very very little current you could see that current is very less.

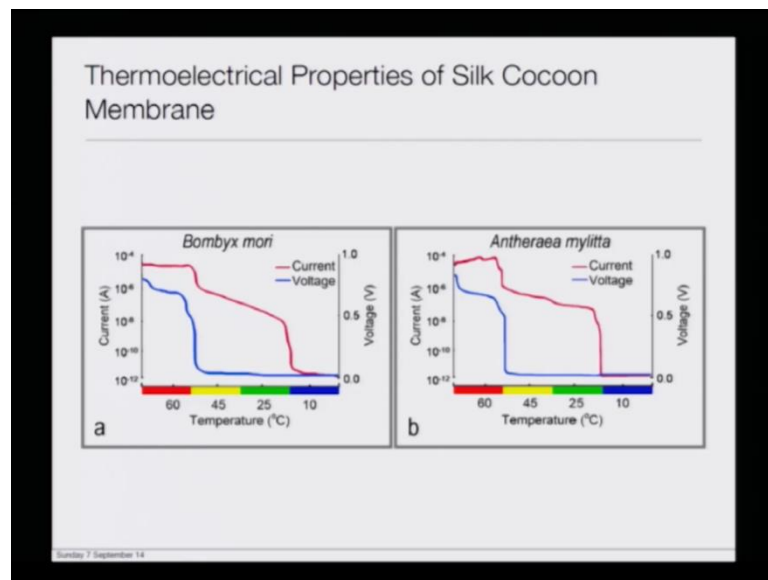
now if there is a moist cocoon, then the current jumps very significantly follow the only the panel a now you de mineralize the cocoon, then also you will see a significant amount of current de mineralization means you are getting a rid of all these x getting rid of the x out. So, it means you are getting rid of a several charge carriers out there now the current density increases significantly, if you see the picture when you are exposing this to water wafer, and if you dope it. Now you are adding n a c l to that kind of you know ensuring the when coming in contact with water what it will do it will form n a plus ions, and c l minus ions what you will observe is the current density goes up.

So, the same thing in the case of anthereaea, if you follow the section c you see the same thing it is pretty much follow the same trend dry cocoon it is almost acting as an

insulating material there is hardly anything, but the very moment there is exposure to moist condition this behaves as if it is a conductor or something like a semiconductor or almost behaves like a conductor. So, if you remember I was telling you all the eshies were follows the relative humidity is at eighty percent or at only at relative humidity eighty percent you see this kind of charge motion, but then you have to realize most of these hornet nest or silk cocoon remain in a area in kind of an micro environment.

Where there the humidity is higher they may be in a shed in a corner or you know surrounded camouflaged by several trees or something leaves likewise you know. So, those kind of camouflaged region have a micro environment where the relative humidity is slightly higher, because there is a transmission taking place continuously from the leaves, and surrounding vegetation, and that kind of increases the relative humidity in that location . So, now, if you see at the voltage trend you again see the same thing at a dry the voltage is low, but then as you moisten it the voltage egos up it means one thing is very, very clear that this kind of situation are wet electricity. This is not something. So, still a question remains who are the charge carriers in this situation. So, this is the first clue in this study that this kind of materials only functions, when it is exposed to or it is kept in a kind of you know high relative humidity.

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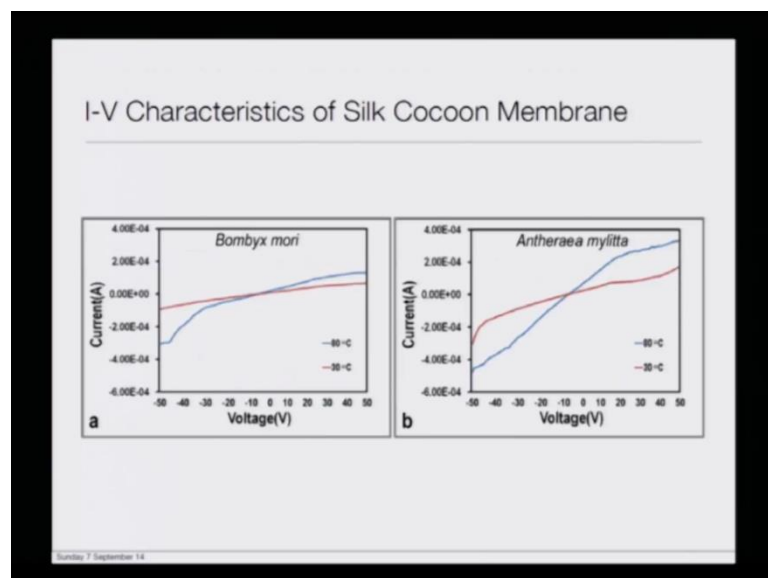
Now, this is a very interesting study to look at what are the thermo electrical properties of it. So, if you follow this graph if you follow the let us follow, because the trend is

same let us fall in the care of bombyx the red line if you see it as you are moving red line is showing as a current as the temperature is increasing at around forty five.

So, there are two rises you are seeing one you are seeing between ten, and you know twenty five, and second you are seeing between forty five, and sixty. So, so around forty forty five or... So, beyond forty slightly around fifty you see a sharp spike of current, and you saw such sharp spike of current in case of species were at around you know thirty one thirty two degree centigrade here you see it at around forty five fifty degree centigrade there is a sharp rise in it spike of current. So, there are two spikes of current, and if you see the same trend.

So, it means this kind of membranes are thermo sensitive membranes first conclusion you could draw, and during thermo this thermo sensitivity leads to generation of electrical currents this is what this slide is telling, and this trend is pretty much the same in the case of bombyx as well as antheraea. So, what I was trying to explain in the previous lecture thirty ninth lecture that these membranes have a thermo thermo regulatory role which is governed by flow of thermal current holds true here if you see that depending on the temperature shifts the thermal current is varying as well as the voltage. So, it has certain thermo voltaic property which leads to thermal current generation.

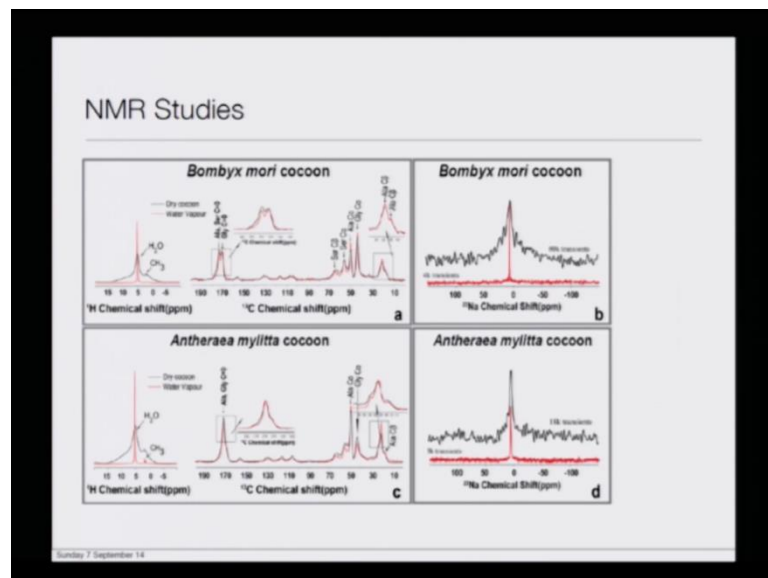
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Now if you see the I v characteristics, and once again for those who have joined late like you can see all these figures in the reference paper I have given you, and if you look at the I v characteristics you will see the current voltage pattern shifts or changes with respect to temperature there are two I v things can be taken at thirty degree centigrade, and eighty degree centigrade, and if you see it the current density is changing as the temperature is rising, and this exactly will remind you what Ishay did if you remember I will just go back to the slide of Ishay is here in the hornet silk it is following the very similar trend what you have seen in hornet the current rises when the temperature rises.

So coming back in the I v studies, that is what is the I v study is telling you as the temperature rises the current rises.

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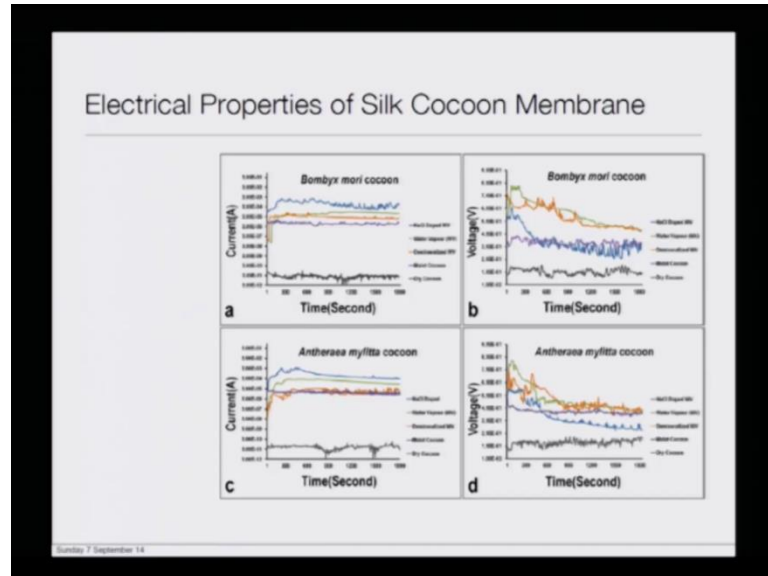


Now, followed by the next study... So, one of the thing is one of the possible explanation for this current could be. So, this what we are trying to figure out could be all these different elements which are present there in the presence of water wafer. So, the water wafer is getting in embedded into this zone I will show you a wonderful model afterwards.

So, these water wafers are. So, they are creating different kind of electrolyte materials you know there could be sodium, there could be calcium there could be magnesium, and likewise at different charges with chloride you know there are others ions, and cat ions

out there, and now since these ions, and cat ions are setting across two electrode of different electro negativity.

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There is a possibility that we may see a charge flow this could be one explanation, but this explanation fails if we look at this picture why in the case of de mineralized condition if you see this picture very carefully on the second panel a see the panel a, and the orange line a de mineralized cocoon, and a moist cocoon you see the same situation why is it. So,, because when you are de mineralizing we are essentially getting rid of all these things getting rid of all of these minus minus these, then where are the ions.

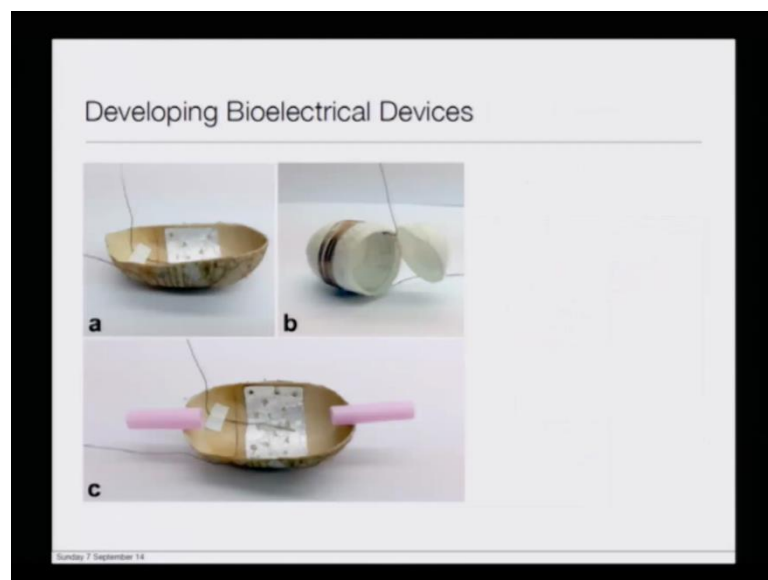
So, that is a very intriguing question, and that is what I we are going slowly at what possibly could be the explanation again coming back to the slide be careful with those that orange line, and the violet line just underneath it you see that orange line which is de mineralized, and getting w b as a water wafer, and the moist cocoon, and the just the water wafer. So, these three lines are very important green line the orange line, and the violet line these three lines are telling you something, and we will be talking about what these three lines are telling you, because in those three lines lies very fundamental phenomenon which is getting orchestrated in between these membrane.

So, coming back in order to see this is a n m r study which has done to see the presence of the water molecules which are present embedded in the silk fibroin matrix as well as the presence of the sodium ions which are present there, and those could be detected

using the n m r out here. So, it is kind of to show that there are ionic species which are present there now followed by we have to went ahead whether these kind of things. So, we have observed that there are you see these kinds of currents are present there. So, at this stage there are two things what will be dealing with what will be dealing with that is whether these currents are dealing efficient enough.

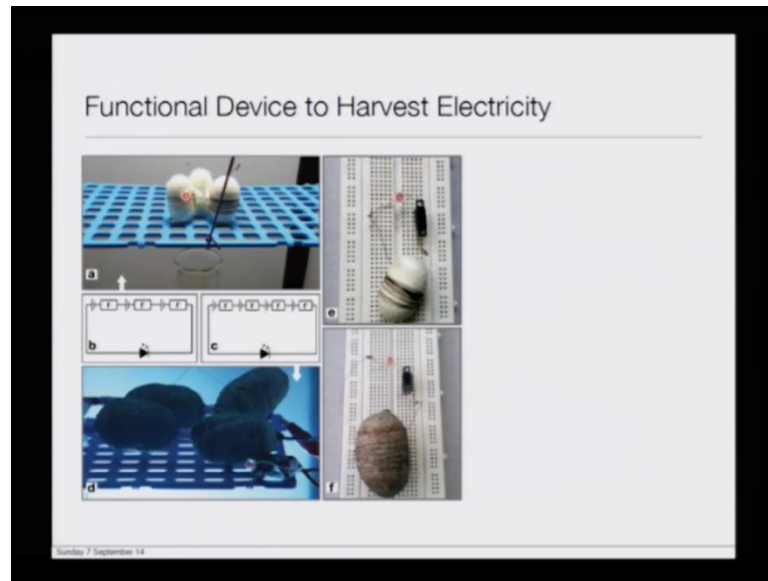
What you see in the slide out here sufficient enough to you know dry some crude devices or you know could you develop some bioelectrical device to harvest necessary energy from a cocoon or not this is one thing. What we gonna answer second thing we gonna answer what are the charge carriers. So, I will be answering this charge carrier thing in the end.

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But first why will be discussing about what are the different devices we can develop out of it. So, here there is some devices development we are talking about.

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So, you take the cocoon you could see in the picture clearly the inside you see there is a aluminum foil which is acting as a electrode, and outside you see the wrapping of the copper.

So, if the aluminum, and copper electrode which are attached across the cocoon surface . So, now, what you see here now when you have this aluminum copper, and you are. So, less concentrate on panel a b c d. So, you have three cocoons out here which are attached by aluminum, and copper, and they are attached in a series circuit, and you are exposing this to water wafer you will see it could it could generate sufficient power to power an l e d light emitting diode where you can do the same thing, but we have just shown it here with four different anthereaea mylleta cocoon if you connect, then in series exactly the way shown it is you can really glow, and l e d out of it.

So, you can harvest some harvest energy by exposing a silk cocoon to water wafer, and water wafer which is at a temperature around on eighty to ninety degree centigrade. So, that is the immune temperature. So, underneath what you see that a beaker coming enough in the panel a from that beaker basically beaker is getting it is it is boiling water which is you know there is there is water boiling, and water wafer is coming out, and in the presence of water wafer what you see is that cocoons started to glow . So, now, the question arises that could we really make very you know this is the very crude device

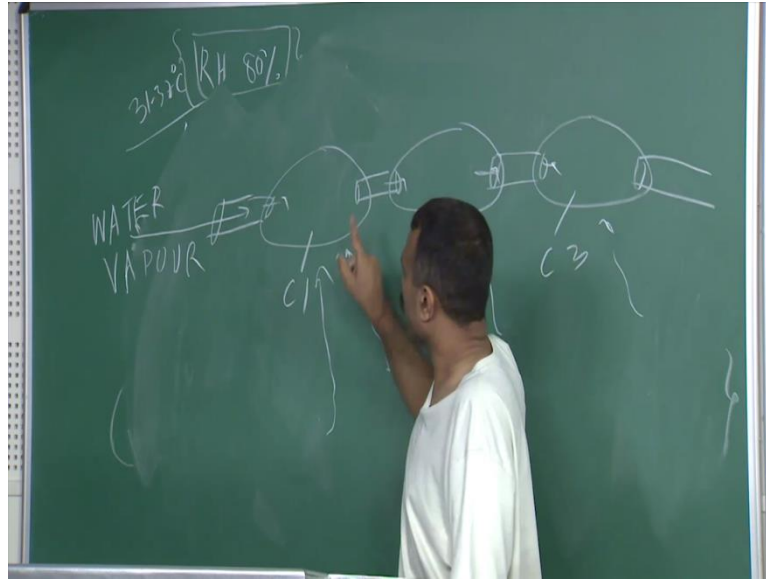
which is exposed to water wafer, and likewise, but could we make a much more finally, device.

But before we get into this just look at these two panels e, and f what does the e, and f is telling one more thing needed to add you can read the paper the reference paper it is free of cost online, and you will come across a series of videos where you will be able to appreciate the whole process how these devices are being used to you know to generate electricity you can actually harvest electricity from these devices, and please go through those videos, because that you will be able to appreciate the whole process much better as compared to you know seeing an still picture out here now what about these e, and f what e, and f is telling e, and f is there is no water wafer on it or anything it is a moist cocoon which is charged for a small period of time using a charger you have these battery chargers or something you charge it.

And then disconnect it, then you connect a load on it you see, and l e d glowing. So, now, you can switch it on switch it off. So, it means the cocoon membrane what we are talking about these proteins which are the assembly which is making the cocoon membrane is acting like a capacitor or a simple charge storage device this one you have to really see the video, then you will be able to appreciate it you can switch it on switch it off switch it on switch it off, and you will be able to you know store sufficient amount of charge in them which could be utilized for (()) applications.

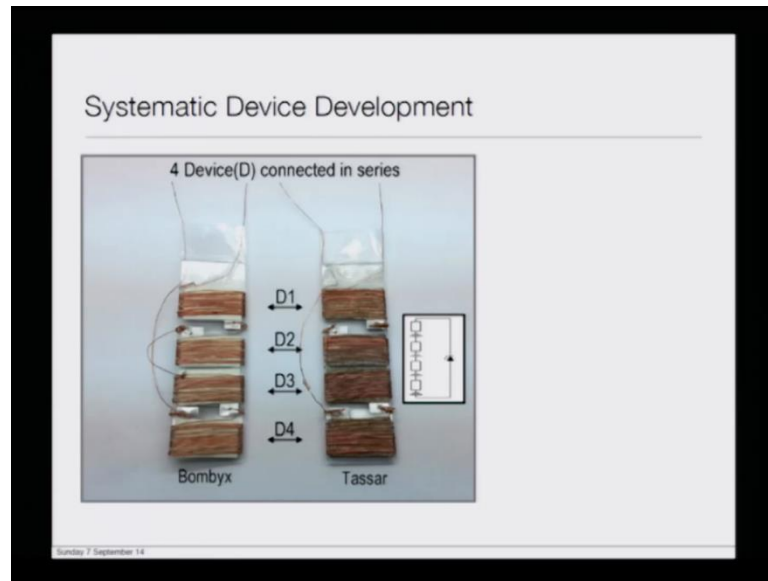
So, this is a functional device from the crude cocoon directly using the cocoon by you know the collect connecting the electrode like this what you see out here you see these two tubes which are coming through. So, you can observe this is by you know by exposing it to elect to water wafer both outside, and as well as inside what does that mean. So, let me just rub the board, and tell you exactly how this is being done I will just keep that relative humidity out there. So, if you have these cocoons connected in series.

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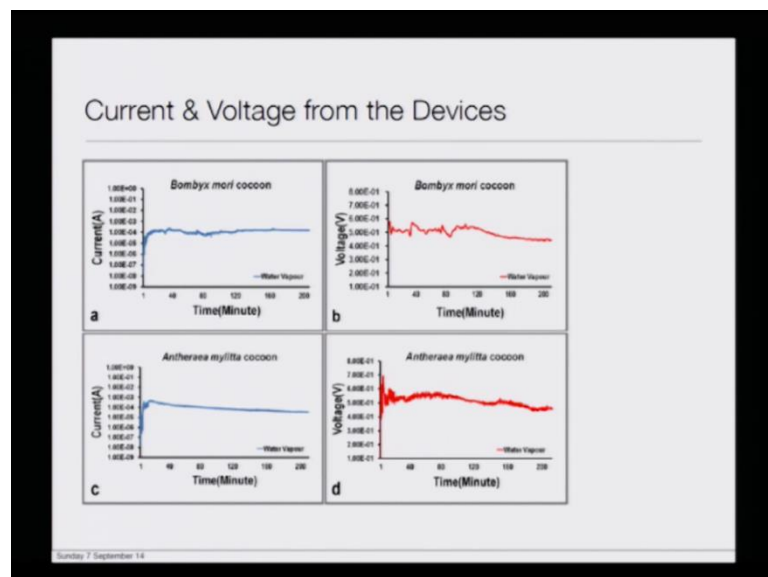
And what you do you have a tube coming like this that is what you observe you know cocoon one c one c two c three likewise, and you are giving water wafer like this. So, there are two ways you can do it either you expose the water wafer like this from outside what you are seeing is that major thing like this. If you see the slide in the panel a you are observing is a water wafer is being exposed outside, and you can even expose water wafer inside like this, and when you are exposing it to inside, then also you see the same effect, but this effect is more pronounce, because your water wafer is concentrated inside. So, it is kind of confined at a space. So, you see this effect you know much more elegantly out there that it generated sufficient power.

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Now, coming to a systematic device develop. So, here you see that the four cocoons were added by you know connecting with these connectors, and likewise, but here what is being done it was systematically you know stacked using two different kind of electrodes. So, this is what you see now where there is a systematic device, and in systematic device also

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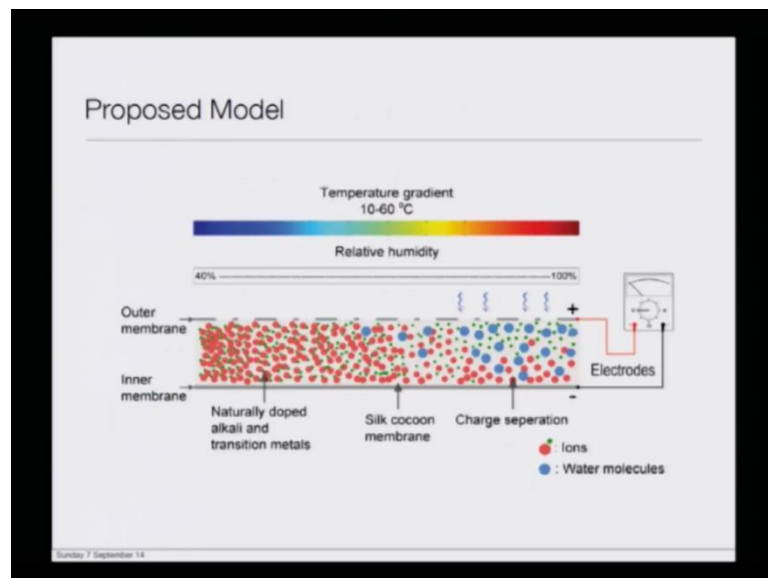


If you see the videos you will see you can see the same kind of you know current, and voltage see these are the current rases what you can see as in the presence of water wafer

over a period of you know two hundred minutes which is almost three hours you see significant amount of current, and you see the, and you see the subsequent voltage in the bombyx as well as in anthereaea.

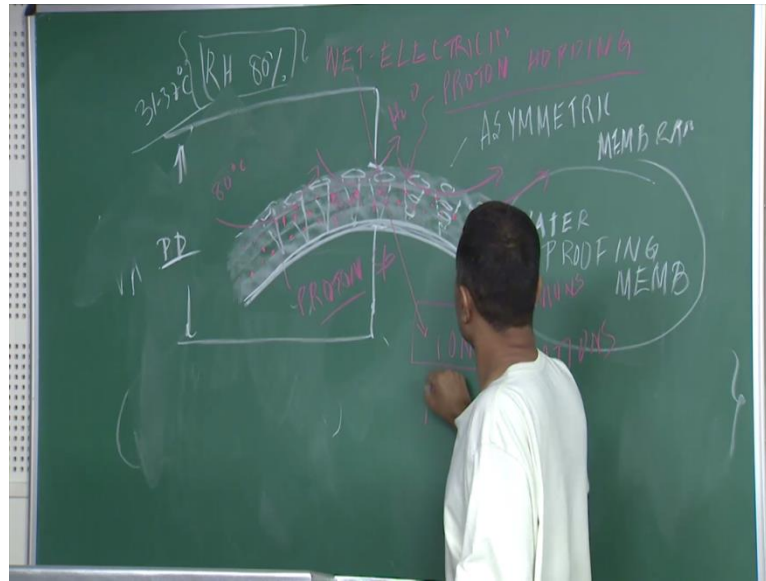
So, what I essentially wanted to put across is that this membrane behaves in a very very interesting way very similar to what has been documented by jacobishay, and that also gives a lot of confidence to tell that what he observed some you know forty thirty or now almost all thirty years back is pretty much the same what we are observing today with much more you know. So, it means the silk proteins cross the genera probably behaves like this they have I mean you can see with certain degree of confidence that at least three of the silk species are showing the same behavior.

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So, these are the current, and voltage of the traces the devices now we talk about the model what is the proposed model currently accepted model. So, you see here there is a temperature gradient tone on the top. So, from ten to sixty degree centigrade likewise, and above now cocoon membrane has been shown as the outer membrane, and the inner membrane you see this. So, you see in the center the outer membrane, and if you see the outer membrane outer membrane as been shown as broken lines it is shown in broken line, because the water absorption from the outside is higher, and the inner part is very, very insulated to water it is almost like a water proofing membrane.

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So, if you really could if this is the cocoon membrane say for example, this is the membrane process of observing. So, there will be lot of bigger pores here through which the water will enter, and then you know, but these pores density changes like this by the time is inside is very, very it is almost like a water proofing membrane this outside. So, this is the kind of gradient you see these are showing the water molecules. So, in other word this membrane is in asymmetric membrane, and because of its asymmetry.

We connect an electrode like this you see a very interesting potential drop across it, and in this asymmetric membrane there are embedded one second there embedded metal ions which are present there an ions, and cat ions sorry which are present there in the presence of water these ions gets activated. So, if you see in this picture in the slide you see there is ions, and water molecules in blue, and then you have the ions which are all scattered across it, and when it is getting efficient water those ionic species based on the electro negativity started to flow across the membrane, but what is interesting to know now I will take you back to this slide.

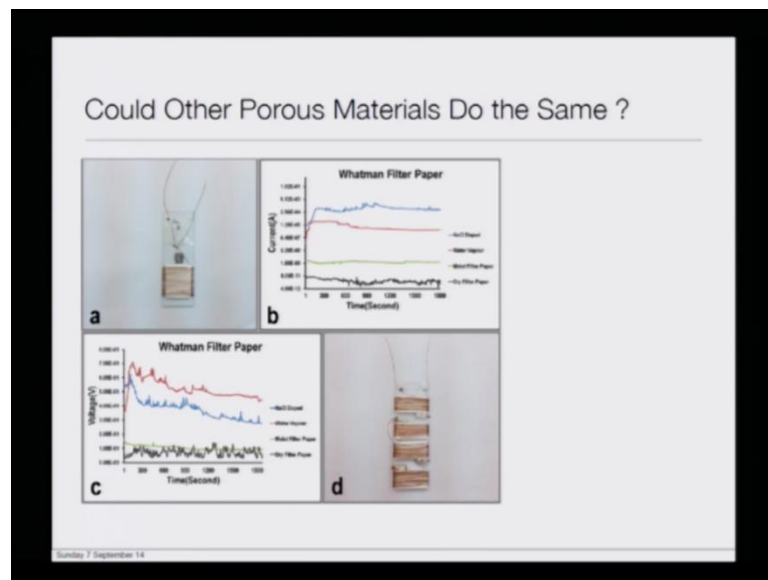
What we what I was telling you that what is the explanation to this situation when you are de mineralizing the cocoon this still you are seeing the same current I told you that please concentrate on the green orange, and the violet line why they are same they are pretty much same this is something very mysterious situation. So, it means there is something else probably. So, even if you remove this remove these red ones still you see

sufficient amount of current how you explain this situation this situation could be explained in a totally different perspective that is something called proton hopping.

What essentially is even if you get rid of all these different ions this particular temperature rezone there is huge amount of at around eighty degree centigrade this huge amount of movement of the water molecules which are taking place on this surface at a temperature of eighty to hundred degree centigrade enormous movement of molecules, and these water molecules are moving, and this is already hydrated there is a lot of proton species which are formed protonic species which are formed there those protonic species possibly possibly could using the word possibly could explain this unusual pattern that even if you are de mineralized cocoon with you or a membrane with you is no mineral still you see a high density of current present there.

So, it means this whole weight electricity what we were discussing is governed by two component one of them is ion which is a charge carrier anions, and one second. Let us go back to the slide anions, and cations, and the second one is protonic possibly these are the two things which are you know governing the flow of current across this membrane.

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This is the most possible explanation, but that takes us it means whether the other kind of membrane could do this similar things, and as a matter of fact to go through the paper what I have recommended you people you will see some of the porous membranes like you know paper.

If they are sufficiently doped with ionic species they could also conduct current this was a back up or kind of you know supporting information what you will see in the paper. So, coming back to the slide if you look at the slide you can see a dry paper is acting as a insulator a moist paper also does not show a lot of current, but in the case of water wafer you see a rise in current, and if you dope it with n a ac l you see even a higher current across it. So, these study is, and this model, and if you go through this slide where as talking to you about the green line orange line, and the violet line of current tells you this is a very interesting zone.

Where both ions, and possibly the protonic species are responsible for the flow of current across these kinds of biological membranes. So, partly where we started in the previous lecture while talking about species studies what are the charge carriers we partly answer this question in this lecture possibly the charged layers are either ions or the protons protonics protonic species shall we call it a biological conductor well I would not be able to answer that question it is it is a material when it is dry when these kind of biomaterials when they are dry they are insulator, but in the presence of water, and varying temperature their behavior drastically changes, and they almost become a conductor, and they generates sufficient.

So, and if you manipulate the physical parameters they sufi they generate sufficient amount of current which could power a low power electronic devices, and the proposed model is shown here, and these are some of the results, and this is the proposed model out here, and you could do the similar thing with porous materials. So, I will close in here, and I will request you people please go through these papers they are very interesting papers from jacobishay.

Now, and there are lot of room for development, and understanding for even a better understanding that how different kind of bi materials could be utilized could be an answer for our question for clean, and green energy.

Thank you.