Nanobio Technology Enabled Point-of-Care Devices
Prof. Gorachand Dutta
School of Medical Science and Technology
Indian Institute of Technology, Kharagpur

Lecture – 21
Strategy for Electrochemical Detection and Tuning of Electrocatalytic Activities (Continued)

Ok students, so, today we will start the again the Tuning method that can be applicable for other electrodes also, right. I told you the tuning method for like gold electrode, gold disk electrode; let us try some other electrode, other materials also. So, this kind of tuning should be applicable for other material. Let us see, this pre-treatment method is it applicable for all or not. So, let us investigate this all the phenomena, so that you will get a general concept for this tuning method, then we will go back again the sensing development.

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So, mainly I will cover today the different tuning method of gold and platinum electrodes, then we will discuss then again the these dependence of the activities on the pre-treatment on this gold and platinum and then their aging effect.

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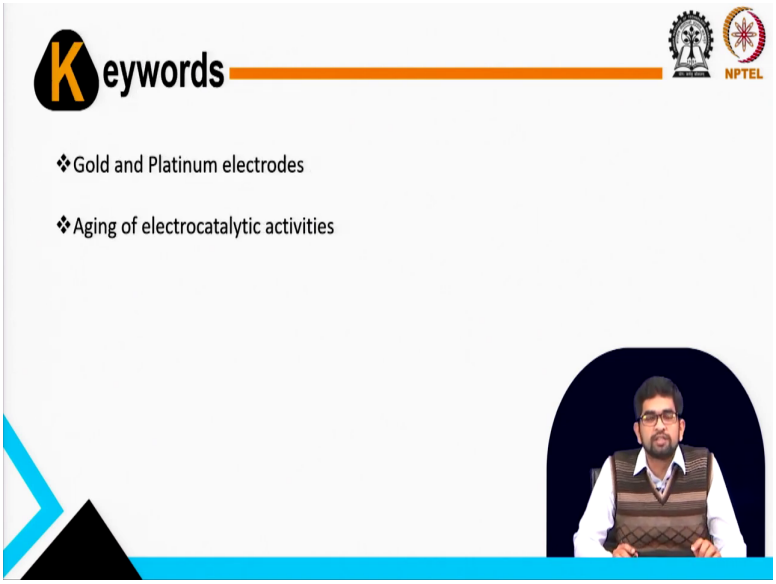

See, main keyword that is why today's topic is the gold and platinum electrodes and there aging effect.

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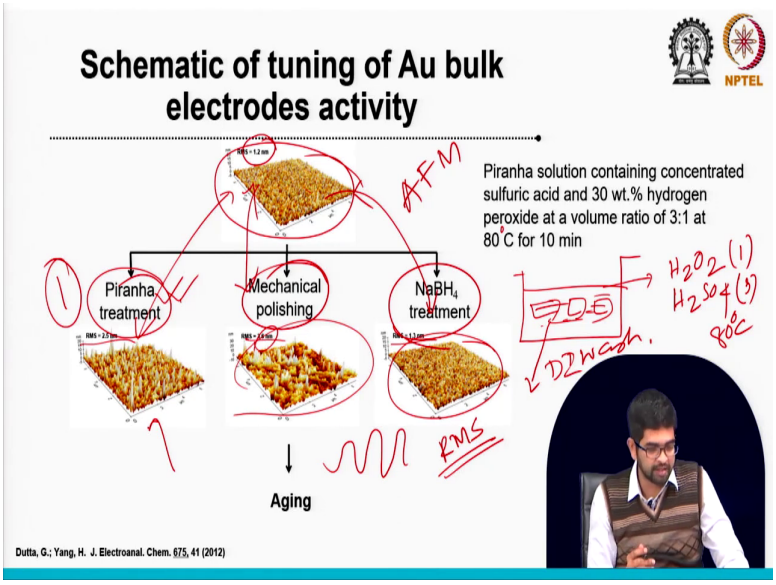

See here the schematic. So, I wanted to show you a basic concept of the different treatment, especially I am saying here the pre-treatment. One is the piranha, another is mechanical polishing and last one is sodium borohydride treatment, ok. So, let us show you. Piranha treatment, it is the solution that contain sulphuric acid and 30 weight percents of the hydrogen peroxide and this mixture is the 3 is to 1 ratio.

And, we will heat this solution for 80 degree Celsius for 10 minute and then we will dip the electrodes suppose for the gold electrode for 10 minute and we will see the surface cleaning effect, there electrocatalytic effect. So, I think you slowly understands that how we can go for the different pre-treatment procedures and let us use them for sensing applications. So, still fundamental all the pre treatment method I am teaching you.

See, the when you will go for the piranha, right. So, for first example is the piranha. So, last class I did not cover much the piranha, that is why today I will cover mainly the piranha treatment. So, what you would do? So, just in a beaker so, you have to take 30 weight percents of hydrogen peroxide and concentrate sulfuric acid; concentrated sulfuric acid and hydrogen peroxide. So, sulfuric acid is 3 and hydrogen peroxide is 1, ok and then you have to heat it in the 80 degree Celsius.

And, this solution there you can dip your small small gold chip electrode and then maybe you can wait for 10 minute and then wash it in the DI water, you have to wash; then check the electrocatalytic activity. Today, I will show you there all the surface phenomena. Means after piranha treatment you can see the surface roughness how changing.

Also, I will compare this piranha treatment with other treatment that I already taught you – one is the mechanical polishings and with the sodium borohydride treatment. See, mechanical polishing case generally we already have seen that surface roughness change, right.

Yield and valley type and after the polishing before the polishing you can see and sodium borohydride treatment you already have seen that surface roughness that is called the RMS value root mean square value RMS. You can see here the RMS 2.5, 3.6, 1.3. So, it is telling about the surface roughness.

Presently, the sodium borohydride case if you compare so, this is the just before the treatment. Before the treatment RMS value 1.2 nanometer and after the treatment it is almost similar. See just for the sodium borohydride case. This is the AFM atomic force micrograph this image.

See in this case the roughness is almost similar. 1.2, 1.3 means we are seeing almost similar. There is no change. But you can see here the 1.2 nanometer the before treatment one mechanical polishing case. This roughness change 3.6 nanometer and the piranha case is changed around 2.5 nanometer and it becomes little rough surface. So, then how it will effect on the electro-catalytic activity?

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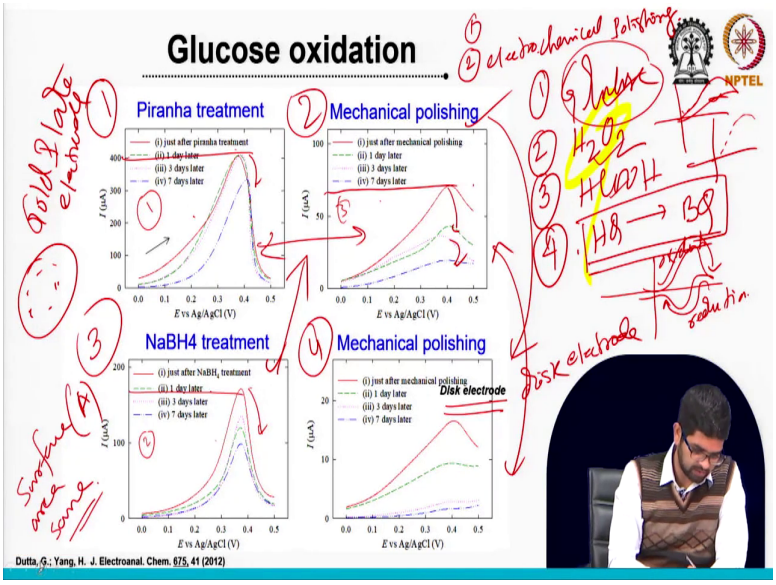

As I told you wanted to check mainly if you want to check the electro-catalytic activity after different pre treatment, let us choose some substrate. So, for example, I told you can choose substrate like you have glucose or you can choose hydrogen peroxide or formic acid or maybe hydroquinone that will convert to benzoquinone. So, this one is almost you can see the reversible peak.

You can remember the cyclic voltammetry; you can see the reverse will almost reversible peak for the hydroquinone like hydroquinone is oxidized to benzoquinone. This is the oxidation and then benzoquinone is reduce to the reduction to hydroquinone again. But, this kind of substrate case we will see it is the irreversible phenomenon.

The glucose case or formic acid case or hydrogen peroxide case they will show like this then it will reduce. So, that is why generally when I will show you the electro-catalytic activity

change let us check there only the oxidations peak. No need to check the reductions peak. So, you can see the glucose oxidation like this then we are not taking the reduction peak. You can consider like this way.

That is why we check the glucose oxidations for piranha treatment case. And then check their aging effect means after the treatment you can store just in the room temperature without when generally you are storing your sensor surface in the lab like this way not the special treatment. Special conditions you are storing let us see the aging effect and how their electro-catalytic activity actually changing.

The interesting thing you can see; so, we will check here 1, 2, 3 sodium borohydride and you can see here two treatment one is 2 is mechanical and 4 also mechanical. So, in this all the electrode here we are using here gold plate electrode for first 3 1, 2, 3 they are the gold plate electrode. And, this one mechanical polishing this one we choose as a gold disk electrode. Ok.

So, why we can say that is why you change this kind of like the plate to disk because when you will develop some chip mainly, we are coating the electrode with some gold, right. We are not using the pure gold. So, that is why we wanted to see all the treatment effect on the coated gold and the pure gold. So, in the first 3 cases in the coated gold you can see the piranha treatment case just after treatment you can see generally, we are getting huge electro-catalytic activity.

But, if you compare the others say it is around the 400 micro amps, but in the other case like mechanical polishing case is too low is this much, see and for the sodium borohydride treatment case it is up to here it is around 180 and for the disk electrode case, but definitely the disk electrode and the plate electrode their surface area different. But that is why you cannot compare this and this, but 1, 2, 3 they all the three cases the surface area same.

So, why I am saying the surface area A, because the current is directly proportional to your electrode surface area See, if the highest surface area definitely because you will get the more active surface for oxidations of your substrate like glucose hydrogen peroxide formic acid

definitely you will get the higher current. So, this 1, 2, 3 case actually still you can see piranha case you are getting the higher current all those surface area same. This is because piranha can enhance the activity much bigger than all the treatment.

Now, let us compare their deactivations. One important phenomena we can observe here that the treatment which help to activate the surface is too high in that case deactivations also slow slowly it will deactivate. See, after 1 days 3 days 7 days it is changed very slowly. Why it is changing? Because we are not taking much precautions about the storage condition, we are simply storing in the lab environment.

So, there may be some change, but that all the causes again I will show you all the factors the contaminations factor, reconstruct there is a reconstitutions effect or not that also I will show you all the XPS study, AFM study. So, from here that one that is why the interesting phenomena is that if your surface is activated highly activated in that case deactivation it is slow.

See, the mechanical treatment cases see these surface area same, but you are seeing that is just not that much activated and deactivation is a rapid. It means the surface was not clean properly and it is actually effecting on your surface deactivations too. So, this is very interesting phenomena right, these two observations.

Again, you can compare with another third conditions that is sodium borohydride treatment. See just after sodium borohydride treatment we can see the glucose oxidations peak around 180. So, it is medium like this one very highest, then second you can say this one second and this one third if you compare the deactivation rate. See sodium borohydride case also it also deactivated, but also not that much rapid like the mechanical.

Means – the mechanical polishings you after the mechanical polishing you may need something else also cleaning. That is why last class also I taught you after the mechanical polishing you can go second step that is electrochemical polishing again electrochemical polishing. What is that electrochemical polishing? Let us I can remind you one more time.

So, let us remove this one. So, I am going to remind you all the polishing steps that us why you should follow just after mechanical polishing because as you know from this behaviour it is confirmed that mechanical polishing is not enough to clean the surface, right.

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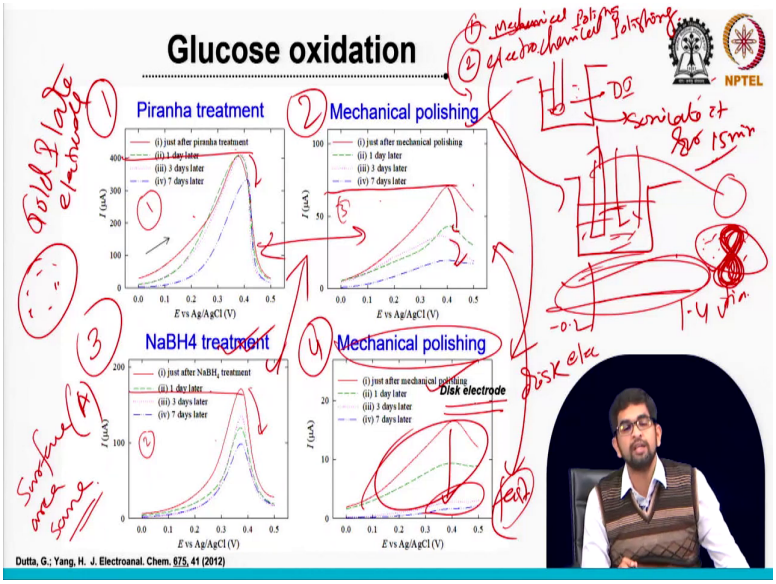

So, first you follow number 1 mechanical polishing. So, it is done. So, after mechanical polishing as you can remember and you have to keep your electrodes in the DI water then you have to sonicate it for 15 minute, then you can wash again the surface.

Then second, you can go take the this is the electrochemical cell one electrochemical cell you can dip your working electrode, your reference electrode and your counter electrode. Then you can connect this the setup with the potentio-stat and potential you can cycle around like minus 0.2 to 1.4 volt and for around 20 times or around 20 times you can potential even cycle

oxidation reduction oxidation reductions. Then your surface will be clean better than mechanical polishing.

So, sodium borohydride case you know already it is very simple cleaning, but still it will not activate completely if you compared with the piranha treatment. Ok but, for the mechanical polishing you can see again so, where we use just a disk electrode you can remember last class, I taught you should have a pad polishing pad here you have to put your all the aluminous slurry.

Then polish it like number 8 like this way you have to polish like this way for around like 1 minute or 2 minute you can polish it and then go through again all the cleaning method and you can check just after polishing then after storage in the room temperature in a laboratory environment you can see the deactivation.

See in this case deactivation also too fast it is very fast. So, that is why this mechanical polishing and pre-treatment then storage for the longer time is not recommended. So, you have to take care of this electrocatalytic activity otherwise you may not get the reproducible data if you store it for the longer time, is very important information's that is why aging you have to keep in mind while you are developing the sensor.

So, why I am teaching nowadays this all the pre-treatment method managing because to get the reproducible surface so that you can develop a reliable biosensor, clear?

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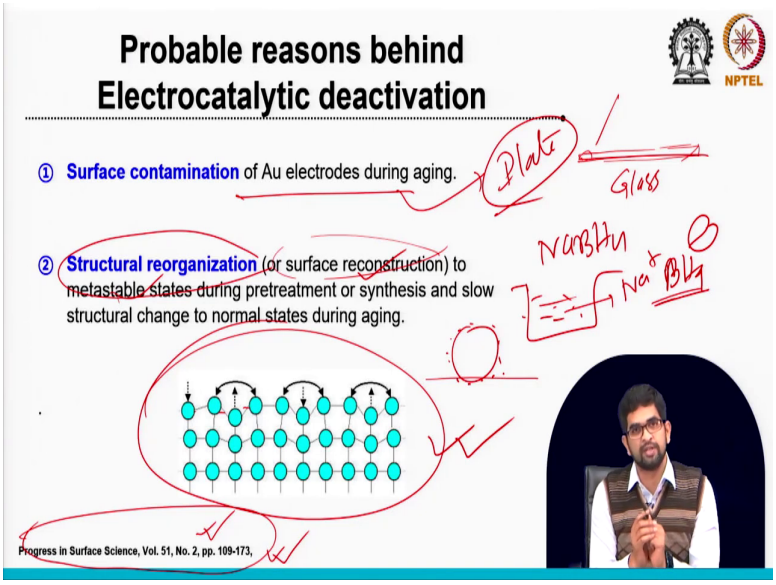

Let us show you the probable reason again I think last class also I told you the surface contaminations today again I will show you all the study has done for the gold electrode. But, in this case gold plate electrode you want to compare like disk electrode and plate electrode also plate mean just you are just you can take a like glass substrate and then you can coat with thermal evaporations maybe some coating you can use the gold pure gold you can coat.

So, on that case we can see the surface contamination now I will show you. The another things in the surface reorganizations or this is called surface reconstructions. So, today I am going to show you the actual structure of the surface reconstructions you can see maybe surface the atom they are organizing themselves after the pre-treatment surface atom after polishing, after sodium borohydride treatment, after mechanical treatment or after piranha treatment so, what happened? The surface atoms they are reorganizing themselves.

So, if you wanted to study more details. So, you can go this reference progress in surface science. So, this is a full elaboration shown is there. So, you can go through this book also, but just try to understands the basic things the surface reorganization surface reconstructions that help to generate some metastable stage. That metastable state during the treatment or during the synthesis I told you know when you will be synthesize some nanomaterial.

So, nanoparticle during the synthesis or just after the synthesis if you measure the electrocatalytic activity it will be very high, right. Then this activity slowly changing so, this is also because of some metastable stage is forming. So, this is because of some surface reconstruction. So, this is the actual explanations of the surface reconstructions or this is just the hypothesis.

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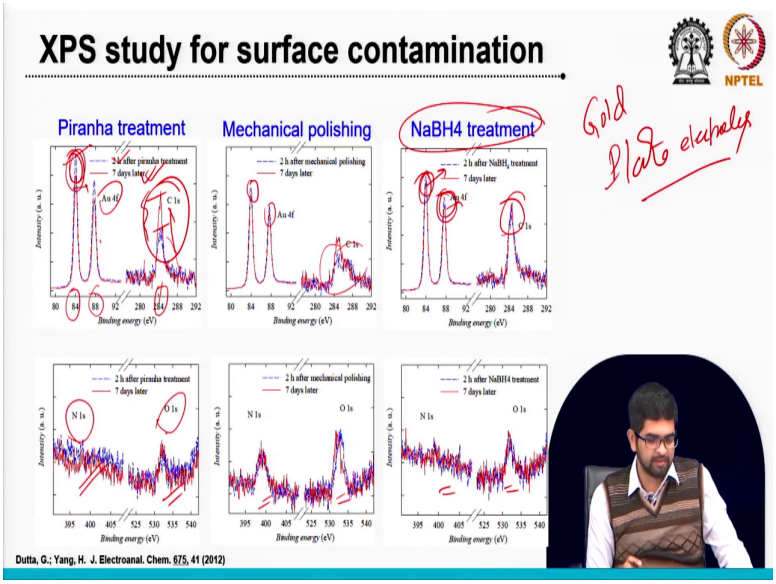

But, let us study some surface characterizations to understand if there is anything else happen surface contaminations or there is anything any material on the surface or not before and after treatment. Just I am trying here all the plate electrode plate this is gold plate electrodes, ok.

If you see the only gold plate electrode just after this three-pre treatment. So, here we studied a photoelectron spectroscopy XPS X-ray photoelectron spectroscopy. You see we generally we are getting the gold peak in this region in two peak we are getting 84 around the 88. So, this two region we are getting gold peak and carbon peak around this region.

You see just after the piranha treatment why I mentioned share after 2 hours because when you are doing some piranha treatment in the lab, then you are cleaning then you have to go to the XPS chamber to I mean XPS room to study these things. So, it may take some time. That is why immediately it was difficult to take the XPS. So, we wanted to see the exact aging effect is there or not.

So, actually we take after treatment or 2 hour we can we took this data you can see there is law not here not that much change, but little bit change still there after 7 days means you can see just after and after 7 days. But little bit you can see still gold peak decrease, right; it means gold peak is covered may be some contaminations may possible because piranha treatment is very very strong cleaning method. It can clean almost all the organic contaminant from the surface.

And, when you store for the longer time like 7 days in the laboratory environment see somewhere this gold peak is covered. So, we thought maybe this is due to not only the surface reconstruction also some contaminations may come, right. That contaminations means generally the organic contaminations where we are thinking. So, we check the carbon contaminations, you see here the carbon contaminations peak just this after 7 days see gold case peak decrease, but carbon case peak increase.

Why? Because gold can be covered with some carbon contaminant, so, gold peak should be decreased and carbon peak after 7 day should increase. Why? Because carbon amount is

increasing so, you can see this much amount I means increasing actually. So, little bit contaminations there that we can tell from this XPS study.

Now, check the mechanical polishing case. You see mechanical polishing case is not that much change we can see because as I told you if you go back the peak here this is not that much actually increase also the activity. So, anyway maybe the surface is not fully clean that we can say right just after mechanical polishing. That is why you can see the if you compare the intensity and their change after 7 days is not that much, but piranha case we can see the clear change.

Why? Because piranha can almost clean the surface that is why if little bit change of the carbon contamination there we can see the change in the XPS study. But sodium borohydride treatment case we can see the golds peak see almost no change carbon peak almost no change. So, let us go back the sodium borohydride treatment case. So, in this case we can see the enhancement here, but this enhancement not due to the cleaning of the contaminant.

This is maybe due to the surface reconstruction. That is why I am saying that not only the reason of the carbon removal contaminations for this activation change, but also the surface reconstructions or surface reorganizations in this factor that is why we assume this factor that sodium borohydride case that we can say.

Although, the surface is not that much clean by the sodium borohydride treatment, but still why we can see the enhancement; this is this called when sodium borohydride treatment we are carrying out in a solution. So, I know the Na plus and BH 4 minus forming and I think I taught you already from this borohydride this hydrogen atom can adsorb on the surface.

And, this hydrogen atom can actually make some metastable stage some strain surface due to this maybe this activations this electro catalytic activations we can improve. So, from this sodium borohydride treatment we can say see the gold surface is not working you can see peak almost not much change after treatment after 7 days, but still, we can see the activity change carbon also not that much change after 7 days also.

Now, let us see the other peak region. This is the complete study of the XPS. Means if you want to study the contaminations factor you have to study this all the region on a main translucent surface or electrode surface. So, first you have to check the main metal that area, then carbon area that you have to check, then you have you can also say nitrogen and oxygen part because the organic material may contain some nitrogen and oxygens also.

So, this region also you can you may see some change or not. You can see nitrogen oxygen is not that much change. So, mainly because of some, but very little change maybe you may see, but not that pretty much predominant. So, contamination is there, but maybe little bit not too much.

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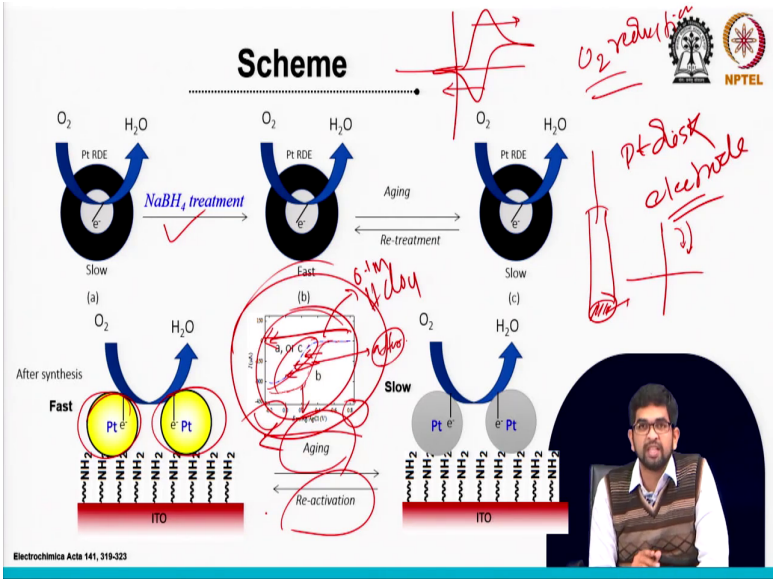

Now, in this scheme I am going to show you how this treatment this pre treatment can effect some other material. So, up to now I here I told you all the studied for the all these all the

things have been studied on gold electrode, right. Now, let us see these all the investigations on another electrode or on another material.

So, that you can check that this kind of pre-treatment or this kind of deactivations procedures that I am teaching you is the universal things or just for very much depend on the very I mean very specific material right that you have to understand. So, here that is why I am going to show you something this kind of pre-treatment method on platinum. Let us see, how platinum effect means platinum electro catalytic activity is changing.

Here I just showed you like this way this is just a platinum disk electrode information's I am going to show you. So, I think you already understood the disk electrode means something it is commercially available, it is shape like this. Here almost the pure platinum we are using. See and we measure here oxygen reduction.

So, you may ask why not you change the glucose oxidations. Yeah, it is fine that is that also you can say glucose oxidations or formic acid hydrogen peroxide another thing, but platinum actually very much active for the oxygen reductions that is why we focus on oxygen reductions.

Means see we wanted to see the aging effect maybe after one day or after few days there is very small change due to the aging effect. So, how you can measure that also depend on how your surface means and your like in this case the platinum how this surface behave during this catalytic measurement like if you measure like oxidations like you can measure glucose oxidations, but this oxidation change peak change the oxidation current change during the time interval may not be that much.

But, here why I choose the oxygen reduction for the platinum case because oxygen reduction is very very much dependent on the platinum material on the your translucent surface and platinum is showing very very catalytic activity on oxygen reductions. So, we choose here oxygen reduction that is why. So, here also we I can I will show you like sodium borohydride

treatment on the platinum and here you can see how rapid this oxygen reduction reaction change during the measurement.

See reduction you can see here one diagram this is the oxygen reductions see we are measuring here from right to left we are measuring from means we are measuring reduction current and this is just the aqueous solutions where we are not using any kind of substrate just aqueous solution. When we for the measurement of the oxygen reduction reaction of platinum we are using perchlorate solutions. So, around 0.1 molar perchlorate solution. So, it is little acidic it is acidic solution.

And, we will scan your cyclic voltammogram from right to left. So, see 0.8 to minus 0.2. You can see this red one this one just after sodium borohydride treatment and then this dot dot blue one this is after aging effect maybe after one way you can see this deactivations means as it is shifted towards left you can see and this oxygen reductions you can see the highest here when this case see this actually shifted towards left after the aging.

So, in this case we can say that this electrode actually deactivated after the aging I think I can show you again like if the oxidations peak shifted towards the right then we can say that surface are deactivating and if reductions peak shifted towards left, then we can say surface actually becoming deactivated slowly. So, you can see the reductions peak for the oxygen case it is shifted for up to the aging. So, we can say the surface actually deactivating.

So, that phenomenon actually I will again I will discuss you more details so, in the next class that. Also, I will check this one for platinum nanomaterial also, that also I will discuss also in the next class again and, how during the aging factors actually effect during the long time storage in the laboratory environment for the platinum particle also that also I will discuss in the next class again. That is all for today's class.

Thank you. Thank you all.