Physics of Functional Materials and Devices

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Lecture – 38, Week 10

Electrochemical Sensors

Welcome to the new week of this course on Physics of Functional Materials and Devices. In the previous week, we have started talking to you about the applications of functional materials. One of the first applications which I started discussing was in the field of sensors. In this first lecture of week 10, let us continue our discussion and see what are electrochemical sensors. So, what would be covered in this week? We will give you the details of electrochemical sensors. After discussing the basics of electrochemical sensors, we will talk to you about the materials which are used in electrochemical sensors.

Why they are used in these sensors? Before the application of these materials in such sensors, what are the basic characterizations through which these materials have to pass successfully before they can be employed in such sensors. And once we know the materials which can be used then how do we fabricate such sensors and finally, we will give you examples of these sensors in real world applications. As we saw in the previous class that sensors are devices which react or respond to external stimuli and also generate a signal which is collected by the processor that processes the signal generated by the sensor and then it gives us meaningful information. So, what would be an electrochemical sensor be? It would be a device that would be transforming the electrochemical information into an analytically useful signal.

So, you would be basically collecting information about the electrochemical reactions which can occur in different types of materials. Based on that information you will process the data and from the process raw data you will try to extract meaningful information that is being termed as useful signal. These sensors are quite versatile. What do we mean by that? We mean that they find large number of applications. They can be used to detect pollutants in water to monitoring glucose level in blood from ensuring the quality of food to optimization of industrial processes.

You can use for detection of vitamin D concentration in blood to the quality of redox activities which are resulting in a electrochemical response in certain environments. So, the basic criteria for such electrochemical sensors would be that they must be cost effective, they must be selective and sensitive and they should be rapid meaning you should be able to switch on these sensors rapidly and you can regenerate it. rapidly so that they can be reused. So, off and on time should be quite small. If you see the various kind of electrochemical sensors that are being discussed and are being routinely used at industrial level, then you will find that the electrochemical sensors can be broadly classified into four such headings.

You can have different classifications also. These are not the only way of classifying electrochemical sensors. But mostly electrochemical sensors are classified as amperometric sensors, potentiometric or voltammetric sensors, impedometric sensors or photo electrochemical sensors or sometimes they are also called as photo electrochemical devices. Let us start with first set of sensors. If you look into the term potentiometric sensors, what would they would be dealing with as the term potentiometric suggest.

It is an electrochemical sensor that would measure the potential difference or voltage between what? This is a fundamental question which you need to answer. So, potentiometric sensors would measure the potential difference or the voltage generated between a reference electrode and a measuring electrode which is responding to the changes in the concentration of specific ions or analytes in a solution. You take a reference electrode why because you measure the voltage with reference to this standard reference potential. These sensors are mostly based on ion selective electrodes that means, they will have redox activities driven by certain ions. It is not that they will be responding to all types of incoming charges ions molecules, they would be quite selective.

Because of this selected interaction, with the target ions the material will generate a voltage that is potential difference which can be measured and the magnitude of potential changes would give you a hint towards analytes concentration. Very easy way of detecting variations in the nearby environment to potentious potentiometric sensors. So, what would be empirometric sensors? If you have understood the first, this is very similar. Here you will have the sensors where an analytical method having high accuracy sensitivity would be used, Where the applied voltage serves as the driving force for the electro catalytic redox reactions. Redox means reduction or oxidation reactions.

Because of reduction or oxidation reactions, you can have the electrical currents and these increase or decrease in electrical currents would be proportional to the concentration of the analyte and therefore, from there you can find the concentration of the analyte. Now, if you have a controlled potential system, then you can build these fundamental instrumentation and you can measure the changes in voltage or current. To measure this change what would be required? You would be basically requiring two electrodes and these electrodes would be submerged in an electrolyte of an appropriate composition and when you have the solvated ions or dissociated ions then you can find out the concentration of the ions in a given electrolyte. But before you can use these materials a very common characterization which these electrodes have to undergo is a three electrode configuration. Here you have three components, you have a working electron, you have a reference electron and a counter electron.

The working electrode is the one where you are going to use these material which you have synthesized and you are coating on a film or a substrate and then using it as the sensing sites. Reference electrode is the one which maintains a constant potential in comparison to the working electrode. Some of the commonly used reference electrodes are AG/AgCl, or Hg/Hg_2Cl_2 solutions and there is a counter electrode. The primary job of counter electrode is to maintain the potential at the working electrode. It is an inert conducting substance and does not react with the electrolyte or the solution where you are going to measure the concentration of the analyte.

Mostly platinum or graphite based counter electrodes are used. So, whatever changes would be occurring would be because of the response characteristic of the active material which is forming the working electrode. This is a typical configuration of a three electrode system. So, you can see three lids coming out. and you have a potentiostat galvanostat which can receive the signal from these three electrodes.

So, reference electrode for example, is AgCl in 3M KCl counter electrode can be used is platinum rod to make a working electrode. these are powders. How will you make powders to interact with solutions? The moment you have powder in some liquid it will get dispersed. Therefore, to make a free standing working electrode you have to have a film out of that. So, what you do? You actually disperse let us say 80 percent of the active material in a solution of PVDF where acetone is acting as the mixing media or the solvent for PVDF.

Then you disperse 80% of your material in 10% PVDF. Now, PVDF being a dielectric will induce some kind of reduction in the current collecting capacity of the mixture. Therefore, to compensate the loss in the current collecting or transfer capacity of the film which will form because of the mixture of PVDF with the active material, what you do? You add 10 percent of carbon. Let us say activated carbon which has higher conductivity, so that you do not lose over current transfer capacity of the film. So, then you make a slurry out of it, you spread this slurry on a substrate and then this substrate is allowed to dry.

Once it is dry you can take out the film and from that film you can cut a working electrode let us say of 1 cm^2 area. So, now, you have a free standing film where the powders will not fall in the solution and you have a active material which is going to sense the redox reactions. Typically, let us say you can use the active materials as 1 mg per cm^2 or you can have higher concentration depends on what type of materials are you using. To calculate the currents what you use? You use the Randles-Sevcik formula which is given by equation number 1. and you can also use Brown-Anson model to predict the value of I p given by equation number 2.

The constants are measured on the right hand side. Using these formulas you can straight away find out what would be the typical currents which you will obtain. By measuring the current you can find out the concentration of the analyte. Let us take an example of functional material ranging from 2D type confinement to 0D type materials to see how these electrochemical sensors work. So, we will start from quantum Well, we can go to quantum wire or quantum dot type structures and you will find that their response characteristics will be different and therefore, they will be used in different kinds of sensors.

Let us take three examples which are very important in today's world. Glucose detection, Vitamin D3 detection. and DNA detection. So, you can use pseudo 2 dimensional, you can use 1D or 0D materials. So, what we studied in week 2 and 3 where we were talking about the synthesis of materials, the nanomaterials, now you will see that they have large number of applications.

Cerium oxide is a functional material which we had studied earlier. In the previous lectures, we had talked to you about the use of hollow structures for various applications. What do we mean by hollow structures? So, if you look from outside they look quite the same, but if you look into their internal structure one is like watermelon. So, it is solid inside and other is like the shell of coconut it has a cavity inside. So, from outside you may not be able to distinguish, but the internal arrangements are quite different and therefore, their surface areas are quite different and the interaction between the analyte and the active material will now occur at two surfaces, the inner surface as well as outer surface of the hollow structures and therefore, you expect that such kind of morphologies for functional materials can become useful for electrochemical detection or sensor.

So, you can tune the morphology. So, tuning of morphology is a way to make new materials and if you have new materials you can have new sensors. Typically these kind of cerium oxide based hollow structures can be easily synthesized using the mini emulsion technique which is oil in water kind of synthesis protocols. You can synthesize cerium oxide hollow structures for this very simple. Sometimes you believe how to make hollow structures.

You just take the disperse and the aqueous phase by dissolving cerium nitrate and polyglycerol polyricinoleate PGPR in weight percent in toluene. Mix it and then just take it to hydrothermal jar, heat it slightly and what you will find that you will end up getting hollow structures. So, very very simple and then you can use it for various application oxygen detection, VOC detection, Vitamin D3 detection, you can use it for various applications. you can use as electrodes in batteries, in fuel cells, you can use it as ion conducting membranes, large number of applications for the same material.

So, this is what you can see. This is the SEM micrograph. Can you see that there are clear cavities in the middle of such particles? So, you can just see the ones which are aligned and facing the beam from there you can clearly see that they have hollow cavities. And if you look the into their TEM pictures they it becomes even more clear is just like the polo candy which you eat. So, you have the formation at the periphery and inside it is clearly having a cavity. So, you have outside wall, then you have the wall and then you have the cavity.

Now, use these materials and just measure the I-V characteristics at different scan rates in presence of the molecule or analyte which you want to detect. For example, in this case let us say we want to detect glucose. Now, if you take let us say 1 mM glucose solution and then you detect it under various scan rate. So, you are changing the rate at which you are changing the current from one side to the other side and working in the potential window where this solution is stable. You can clearly see that the area under the curves change and you have clear signatures of anodic and cathodic peaks which are occurring at 0.

32 and - 0.23 volts respectively. So, at one point in the forward direction you are having an anodic reaction in the reverse direction you are having a cathodic reaction that means, system is undergoing reduction and oxidation processes. Clearly as you will change the concentration of the solution the reaction will change and from there you can find out the typical reaction kinetics and you can also find out what is the average surface concentration of these hollow CO_2 that are going to interact with glucose. and you will find that that value is significantly large that is of the order of nearly $3 * 10^{8}$ mole/cm^2 You can also find out the average surface concentration and you can find out the electroactive surface areas from the Randles-Shevzik formula. What are we supposed to do? We are basically required to determine the limit of detection and limit of quantification that will decide the application of your sensors. What you do now? You take the CV curves that is the IV curves as a function of changing glucose molecule concentration.

You will find that there would be a linear relationship between concentration of the glucose and the peak currents which you obtain and the typical correlation coefficient which you will get is of the order of 0.98, 0.99. So, very good fit and estimation that there is a linear relation. You know limit of deduction is defined as 3σ / S and limit of quantification is defined as 10σ / S , where m is the slope of calibration curve and σ is the standard deviation of the blank solution.

So, if you see the values of the blank solution and then compare it what you are getting, what is the typical variance you are getting. In this case you will find that LOD and LOQ were found to be 6.5 approximately and 22 nM respectively. That means, you can go to very low level and you can detect presence of glucose in very low concentrations also. nM generally you talk in terms of M maybe mM, but now you are talking in terms of nM and you can go to very low concentrations and clearly without any problem detect presence of glucose in a solution and that is what is being done in most of the electrochemical sensors.

So, very easy now to make a sensors you can now change material and you can use it for different kind of sensing application. Let us say we now go from a hollow structure we go to a carbon nanotube. So, a tubular morphology and see what the application would be let us see a very common detection which is being asked by the users to find out is the vitamin D in blood or vitamin D3 concentration in a solution. So, you first have to simply make carbon nanotubes and to improve its reactivity. Let us say you want to dope it with nitrogen.

So, you take the carbon nanotube which are available in the market and from the vendors and then you just put it in a hydrothermal and you will find that you can actually have doping of nitrogen in such systems. So, you just need a source of nitrogen which will get adsorbed on the surface of CNTs. Then you take the X-ray diffraction and you will find that the high intensity peaks will give you the lattice planes which are expected from a layered structure for example, 002 and 100 lattice planes of a graphitic structure. Then you find out the morphology clearly you will see it is a tubular morphology. and then you can also take a TEM and from TEM you will find that these morphologies also have a cavity in the middle.

So, you carry out such kind of measurements and you will find that typically you have these tubes which can be very very long that is 100 µm, 200 µm, but the inner diameter of these tubes are of the order of 20 nm and so, they qualify to be called as nanomaterials. Then you take the XPS data. X-ray photoelectron spectroscopic data which will confirm that it is nitrogen doping that is occurring on the surface of the CNT and from there you will get presence of nitrogen signals and you will get modifications in the carbon or oxygen which are on the surface and there you will find that there is some interaction between nitrogen and oxygen in CNTs or nitrogen and carbon which is leading to the modification in the overall response characteristics of the sensing element. Then you measure the BET surface areas, the Brunner Emmett Taylor surface area which is an adsorption desorption based analysis, we will talk about this in weeks 11 and 12. you can find out the typical surface area of these sensing materials.

After that you carry out the same kind of measurements. So, you have the I-V curves, then you plot the Randle-Sevcik equations . And from the slopes you will be able to find out the limit of reduction and limit of quantification and you will see here you can even detect much lower concentrations. You can go up to 16 pM concentrations of vitamin D3. in a solution and you will be able to detect it whether it is present or it is not present and limit of quantifications are in of the order of somewhere between 4 1 to 4 nM.

So, very very sensitive electrochemical sensors. Now, you can carry out the same measurements by having systems where you are using the nitrogen doped carbon nanotubes in combination with another redox mediator. So, that the charge transfer are much higher and you will find that you can have very high switching on and switching off times in sensors also. If you compare these measurements, you should be able to claim that this sensor is actually selectively reacting. So, then you characterize it with different molecules in the solution. For example, you characterize it vitamin D3 with glucose with formaldehyde with elastin or any other molecule.

You will find that the response characteristics if you normalize with respect to the one which you got for vitamin D3, the others have much lower response and therefore, it is called that such sensors are quite selective also and they are stable also you can use them continuously for 60 days or so. So, if you have a cheap sensor which has very fast off and on time and it can be used n number of times for 2 months or so, then you have an very useful and economically viable sensor. Finally, let us go to quantum dot level and see how they can be used to detect DNAs. So, then you make quantum dot structures.

So, confinement in all the three dimensions. So, all the three dimensions are in the range of 1 to 100 nm and you use the basic characterizations once again to confirm the formation of quantum dots. So, XRD, TEM, Raman and you have XPS. What will you do? Same measurement very very simple and similar you will have the current voltage measurements then you will plot the change in current as a function of concentration of DNA and from the slopes you will find out what is the LOD of these materials and you will find that using the quantum dots based on graphene. you will find that you can detect DNAs as low as 2.

03 nM as well. And this is clearly talking in terms of 10^{-9} and hence they are very very sensitive electrochemical sensing elements. So, I hope now you are clear that one of the applications which are there for functional materials is in the field of sensors and the same material can be used in different types of sensors. by changing the morphology of the particle or you can use different types of materials and you will be able to make different kinds of sensors. So, it is not necessary that there is only one type of material which will

be used to make glucose sensors. You can fabricate design any other material also and make a glucose sensor.

It is only that you must ensure that it is safe, secure, selective and sensitive over a long duration so that the data which you get from it is reliable and can be given to the end user without any hesitation. To develop further understanding you can refer to these publications from my research group which and if you go back to the references mentioned in these papers you will also get details of other relevant literature. Thank you very much for attending lecture number 1 of week 10. Thank you very much.