

Physics of Functional Materials and Devices
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Lecture 41

Magnetic supercapacitors

Welcome again. In the previous two lectures, I have talked to you about supercapacitors and you would have seen that we have talked to you about the use of metal oxides, carbons in developing pseudocapacitors or EDLCs or a combination of two. In this course we are talking about functional materials and devices. Till now we focused about the use of these capacitors mostly for charge storage and when there was a field that is electric field that was applied and these materials were leading to some kind of a redox reactions and you were seeing a storage behavior in the device because either there was formation of double layers at the interface Or you had the redox that is reduction or oxidation reactions taking place leading to appearance or extraction of charges from the materials. We want to talk about functional materials and devices. So, let me give you a proof that these devices which are based on these functional materials are also becoming very important functional devices.

Let me take one of the examples and explain to you why they are becoming known as functional devices. We have seen that supercapacitors mostly were being used where you were applying electric field. Have you ever heard that there are also magnetic supercapacitors or magnetic capacitors? Let me show you how a new field is emerging which is becoming very important and that is called as magnetic supercapacitors. These capacitors are the ones which respond to electric field as we have seen along with that it also responds.

To the applied field. So, you can have very strong response as a function of applied field. So, they are called as magnetic supercapacitors. As you saw that by changing the morphology of the particles you can tune the storage capacities of the devices. Let me ask you a very interesting question which some of you may have thought during the reading of the relevant literature which I had mentioned in the previous class.

If you look into these materials for example, iron oxide or copper oxide or cobalt oxide you would have seen that we are talking about materials which have a magnetic element in it. Iron oxide iron in it, cobalt oxide cobalt, manganese oxide manganese. chromium oxide, chromium. So, you have these ferromagnetic elements forming an integral part of this solid solution. Along with that you can also have dia or paramagnetic materials which are being used in such kind of systems.

So, very simple question which needs to be asked and was not asked till few years back was what will happen to these materials and their redox property if they are asked to perform under the application of magnetic field. Will their redox properties change and if they do what would be the impact of the changes on the storage capacities of the corresponding energy storage devices be it be super capacitors or batteries that can be fabricated using them as an active material. We will see later that even the lithium and batteries which you have in your mobile phones, in your laptops, in your smart watches they have for example, lithium ion phosphate, lithium cobalt oxide which are commonly used electrode materials. That means, there is an element which is ferromagnetic. Therefore, have you ever thought of that what will happen if the batteries are made to function near the environment where there is a magnetic field.

You will be quite shocked to know that even the batteries can have very different response characteristics if they are made to operate near weak magnetic fields also. I am talking in terms of not Tesla's in terms of few Gauss. So, even small magnetic fields can modulate the properties of such energy storage devices. And the reason is that you have a magnetic material which is being used to fabricate the device and you have seen in the week how you can tune the magnetic properties of a material. And if you move from large bulk size materials to small elongated grains type magnetic structures, then the magnetic behavior is also quite different.

As a result, what will happen? You can also expect significant modulation in the response characteristics that is the electrochemical properties of such materials which have a magnetic element as one of the basic constituents. So, when you move from a large sized materials that is bulk to smaller size. There is a new class of materials which are becoming very important that are called as 2D materials. For example, you can have 2D maxines and these materials are also finding use in applications ranging from energy storage to 5G antennas to EMI shielding to biomedicine to sensors to optoelectronics to environmental applications for water purifications or removal of pollutants. And all these materials which we are going to talk about or we have talked about in last few lectures you may have seen that you can tune their morphologies.

You can go from bulk to nano size, you can make hollow structures which are also called as pseudo two dimensional structures. They are called pseudo two dimensional structures why? Because they simulate the behavior of two dimensional structures even when there are three-dimensionals which have to be considered while explaining the formation of such hollow structures and therefore, they are called as pseudo two-dimensional structures. If I now look into these materials once again with this two figures in front of us which have been taken from the reference cited above, you can clearly see that The range of applications for such materials are immense and not only two, but they are much more than two applications making them a functional material and let us see how we can now make functional supercapacitors that means, now we are going to use supercapacitors for

determining or detection of magnetic fields. As you know what happens in supercapacitors? You have the two electrodes and when you apply the field you have the charge storage at the boundaries and because the distance between the positive and the negatively charged solvated ions are in the order of nanometers or so. So, if you calculate $\frac{\epsilon_0 A}{d}$ then the d value becomes extremely small A is the surface area.

So, if you use the nanostructures you have extremely high areas or the contact area which takes part in the storage or formation of layers. So, A is very large, d is very small and hence C will be extremely high. So, this is a typical mechanism which we had discussed in the previous lectures. Let us take another example because this is an example which I took during the biosensing class is of the use of cerium oxide. So, cerium oxide can also be used as a supercapacitor electrode material.

You can go from solid structures to hollow structures. And you can clearly see these specific capacitances which we are talking about are in the range of somewhere 175 to 200 farads per gram for hollow structures to around 75 farads per gram for solid structures. and they vary as a function of scan rates, but these values are not small. Please keep the reference as the conventional capacitors. Conventional capacitors are what? They have these values in the range of millifarads to microfarads.

Now, you are talking in terms of farads to few hundreds of farads. So, the minimum increase which you are talking about is of the order of 1000 times or more and therefore, you have very high impacts of these super capacitors on the storage capacities. Let us take another example. Initially, we were talking about only spherical solid structures. Is it true if you take a rod like structure.

There also you will find that when you go from tubular structure to solid rodlike structures, the behavior is very different and you can have still very high capacitance values. But, as expected the tubular that is the one which has cavity in the middle base structures are giving you much higher specific capacitances. Same is true for iron oxide, you have much higher specific capacitances in the hollow structures. These three examples along with what I had discussed in the previous class is slightly repetitive. Why am I repeating certain aspects? Just to show you that you have these electrode materials where one of the elements is magnetic.

What will happen? to these materials if they are made to operate under the field that is magnetic field now. That is where the area of magnetic super capacitors have come to the forefront of research. It gives you two advantages. it gives you the advantage at you can use super capacitors to detect the appearance or disappearance of magnetic field. So, you can use super capacitors that is an energy storage device for application as a sensor.

So, the device itself becomes a functional device one is storage capacity other is sensing

capacity. The second you can tune the magnitude of magnetic field and modulate the storage capacity. Because, if the redox reactions are changing by the application of magnetic field what will happen? You will be able to modulate the storage capacity of a device. So, there are various ways in which you can understand this very interesting scientific problem. undertake the magnetic field-based studies.

Let us again take similar materials cerium oxide or iron oxide-based materials. Are they magnetic or not? What are we going to perform before claiming that these materials are magnetic you have to have the M-H curve that is the hysteresis loop. Conventional study carried out before you can show that a material is magnetic or not. Even though a very weak opening of the loop there is slight opening of the loop. but predominantly you have a superparamagnetic type behavior in these systems.

This curve shows the hysteresis loop for copper doped cerium oxide and the typical curve is that of a superparamagnetic and you have studied earlier that superparamagnetic is coming in because of the concept of elongated grains which appear when you have very small size particles and if you make nano size particles or hollow structures of these materials you will expect such kind of hysteresis loop. So, the basic physics of magnetism at nano scale holds good. Now, what you do? You make a device out of it. You make a supercapacitor device out of these materials. So, you have let us say a symmetric device, you have on both sides' cerium oxide.

If you have something which is called an asymmetric device, you will have on one side cerium oxide, on the other side you can have carbon base electrode and then it will be called an asymmetric device. you will have a hybrid supercapacitor which is formed. So, symmetric device both the electrodes are similar, if it is asymmetric the electrodes are different. For example, in this case let us say we made a symmetric device. What will happen? You hang it in between the poles of the electromagnet, then you switch on the current and you have the appearance of the magnetic lines of force.

Now, you have the magnetic field which is getting stabilized between the two poles in between there is the device which is hanging. Most of the theories which you will read on supercapacitors never considered the role of magnetic field. So, the force acting on the device would always be considered as the force that is qE , but the moment you have the appearance of magnetic field there is an additional component which would come into picture. What would that be? That would be the Lorentz force and that would be given as $qE + q(v \times B)$. Now, you have an additional component and if there is a system which is responding to B that means, the second term which was being ignored when only electric field was being considered as the driving field will come into picture. And if that comes into picture that means, the force which is being felt by the ions which are flowing towards the electrode surfaces would get modified and the electrolyte which is getting intercalated within the surface of the electrode will also experience different force and because of the

change in the magnitude of the force what do you expect? There would be different kind of diffusion mechanisms which would take place and if you have higher force because the second term has come into picture which is additive in nature that means, you will have higher force which is forcing the ions to go inside the electrodes then you believe you will have higher storage capacities. So, your diffusion will also improve and that would impact the storage capacities. Let us see what actually happens. Same measurements, what are the measurements? We will carry out the cyclic voltammetric studies that is the IV studies and the CD studies that is the charging and the discharging studies of the device under the application of a magnetic field.

You can change the field you do not need to change at higher steps. So, you need to change it at small step intervals. So, you know what is happening. For example, the graph A and B show you the variation in the nature of the CV curves or the CD curves at low fields such as 50 gauss, 20 gauss, 100 gauss, 75 gauss. So, you can see these are mentioned in the legend of the graph.

Clearly what you see that the nature of charging and discharging is getting modified. as you increase the field you are seeing that the discharging cycle has a different nature. That means, your storage capacity is which there is getting modulated. So, if you plot specific capacitance at different scan rates again under the application of magnetic field the data gives you the same information. What happens is that when you apply the magnetic field it is showing or leading to improvement in the storage capacities of the electrode materials.

So, if I have to make a magnetic sensor based on supercapacitor. What should I do? I should choose a material which is responding to the magnetic field which we want to detect, use that material to make a supercapacitor. Before making that device you must check that the material which you are choosing is electrochemically active. Then only you will see some behavior in the electrochemical measurements. So, now, you must choose a material which is magnetically active, electrochemically active.

Make a device out of it. Once you make a device out of it, how that can be used as a sensor? if you see a particular CD curve or the CV curve at a given 0 field, then you have a given condition where the field has changed and now you have 20 gauss. These systems are very fast response systems. So, they will show immediate change in their response characteristics. It does not need lot of time to actually show modulation in their response characteristics. So, you will immediately see that the response curve will start changing and if that happens you will find that the material has indicated had there is a new field that is the magnetic field which has come near its environment that is leading to the modulation of the discharge curves or the CV curves.

So, immediately your device is going to become a sensing device, a device where you are believing it is a storage device is now also becoming a sensing device. And that is why you

have seen we have moved from sensors to energy storage device and now both of them can also be coupled to make a new range of functional devices. What is the next logical question you would ask? You would ask that we have talked about solid structures, we have talked about hierarchical structures, we have talked about tubular structures, we have talked about hollow structures, cactus like, rose like, 2D structures, will these materials also show different response under magnetic field and if they do so, what will be the impact on the storage capacity or the sensing capacity of the magnetic supercapacitors. As you have understood during the lectures where we talked about the Stoner-Walsfarth model and the concept of elongated drains. As you change the surface of the nanoparticles, the magnetic response also changes because the nature of the elongated grains will change.

If this happens, it immediately means that the surface area which will come into picture during the charge storage mechanism or charge exchange mechanisms in EDLCs or pseudo capacitors respectively will also get modified. And if that happens if the surface area changes the electrochemical response would also change and that is a new way of making a new range of magnetic supercapacitors or supercapacitors which can be used for sensing applications. So, what you need to do just choose any material and by choosing any material let us say for example, iron oxide you choose that material and make different types of particle morphologies of these systems. and if you use the system to have different particles. For example, you can use it for hollow structures, you can use it for solid structures, you can use for rodlike structure tubular morphologies and then carry out the similar performance that is their specific capacitance determination as a function of applied magnetic field.

You will find that again the response changes and you have new series of magnetic supercapacitors as well as magnetic sensors based on supercapacitors. So, that is why this opens a new range of applications for the functional materials which you have studied. So, what have you seen till now? You have seen cerium oxide, it can be used for biomedical applications, biosensing applications, it can be used for storage applications, it can be used in magnetic fields sensors or they can be used even for catalysis you will see in next few lectures. That is why these materials such as iron oxide, cerium oxide, tin oxide or transition metal oxide base materials are important class of material that are called as functional materials and they are extensively used in functional devices. You can choose the material; you can modulate the synthesis protocols and you can then get various types of functional devices.

I hope these three points were clear after today's lecture. You can look into these references to understand more about the topics which were covered in today's lecture. Thank you very much for attending the third lecture on supercapacitors. From next lecture, we will move on and talk about the field of batteries and why they have become so important in today's world. Thank you once again.