

Physics of Functional Materials and Devices
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Lecture 40, Week 10

Supercapacitors -II

Welcome to the second lecture on supercapacitors. In the previous lecture, I introduced to you the concept of supercapacitors. Prior to that, we had discussed about conventional capacitors and why energy storage technologies are so important in today's world where we are moving towards the renewable based energy landscape. you would have seen that supercapacitors are what they are electrochemical devices which are considered as high-power devices that means they can deliver energy at very fast rates along with that you also heard the term that these can store large amount of energies and deliver them in short period of time. And this period of time can be modified depending upon the requirement of the end users. The importance of these supercapacitors are immense.

They are finding applications ranging from your mobile phones to e-vehicles, to engines, rail engines, locomotive engines, to Formula One cars. There is a proposal where companies are now investigating the use of supercapacitor-based packs to run the buses. Why? Because they can deliver significant amount of power and they can also store large amount of power in much smaller volumes. Yes, the question which will be asked is, but the self-discharge of a capacitor or capacitive systems are much faster than that of batteries.

You can also say that their energy densities are much lower. That is where the companies are proposing to exploit the advantage. What is that advantage? The advantage is that these capacitors can also be charged at a very fast rate. Therefore, the strategy which is being proposed is that as you move from one charging station to the other, by the time the passengers are getting down or boarding the bus or the e-vehicle which you are considering, the capacitors can be charged by the charging stations which are already installed at such stations. You can operate large buses to smaller taxis where the movement is for shorter distance and you will have periods where the vehicle will be static.

That means you will get time to charge these systems. In the previous class, I gave you an introduction on the concept of electric double layer capacitors. What were those? They were basically the ones where you were using the carbon-based materials to have capacitive action. Those kinds of capacitors have much lower power densities and you have saturation limit because the carbon structure cannot be modified significantly. So, you cannot reach very high energy or power density values.

That is where the development of next type of material. materials those are called pseudocapacitive materials was initiated and the capacitors which are based on such materials are called as pseudocapacitors. Then came the term hybrid capacitors. As the name suggests, hybrid capacitors are a combination of EDLC plus pseudo capacitors. In this lecture, you will learn more about the EDLCs, the pseudocapacitors and hybrid capacitors.

Once again, you will find that the capacitors are mostly characterized or named after the type of materials which you use. So, it is again the role of the electrode material which becomes very critical in defining the performance characteristics of these energy storage devices. There are various physiochemical properties of the electrode materials which we need to investigate and study. In the previous lecture, you heard about the cyclic voltammetry and charge discharge studies and how do we use them to characterize the electrochemical properties of these materials. So, we will continue using those protocols and understand the electrochemical properties of electrode materials before we start talking about the final device.

In this lecture, I will also talk to you about the way we would be making the electrode films. So, you will see some videos where you will be able to understand how these structures are actually fabricated. So, let us continue our discussion on supercapacitor electrodes. As you must be understanding by now that the EDLC type systems are the one where the storage is in an electrostatic way. It does not involve any charge transfer reaction.

So, these are non-faradic type materials which are used that mean there are no charge transfers. Typical examples are activated carbons or other forms of carbon-based materials, be it be graphene, be it be reduced graphitic oxide, you can have carbon spheres, carbon nanotubes, you can have carbon sheets, graphite. So, they are typical examples of EDLC type material and they are used in EDLCs. Then comes the next type of device, that is the pseudocapacitor. Here, you move from a non-faradic type mechanism of charge storage to a faradic oxidation reduction type reactions where the charge transfer takes place and that leads to the storage of the charge at the electrode surfaces or within the electron.

So, you must have redox type materials which would undergo such kind of faradic reactions. So, the materials which are becoming quite useful nowadays are based on transition metal oxide, transition metal oxide means these are the materials which are based on transition elements and because of that they have different valency states and because they can toggle from one state to the other, you can either accept electron or give electron during the redox activity and hence you can have the oxidation reactions or reduction reactions whereby you can ensure the charge storage. You have new types of 2D materials such as metal sulfides which are coming into picture and along with that there are flexible systems like conducting polymers which are also being used in such pseudocapacitors. So, as I explained in the introduction of this lecture, Hybrid capacitors are the ones which are

a combination of two types of systems, the EDLC type and the pseudo capacitive type materials. Therefore, what would be the hybrid type capacitors? One of the electrodes will be made up of EDLC type material and the other would be based on the material which can undergo the faradic type reactions that means the pseudocapacitive type.

Materials and then you believe that the advantages of both EDLC and pseudo capacitors can be combined and you can reach higher energy densities while maintaining higher power densities in super capacitors. So, what would be the typical strategy? The typical strategy would remain the same. you would first choose the material which you want to use in these devices. And depending upon the choice of the material, the properties would change and then the response characteristics of the capacitors will also change. There are various protocols by which these materials are fabricated.

They can be bottom up or top down approaches. We have discussed many of them in this course. you can read from the chemistry books because we cannot spend too much time on discussing each and every synthesis protocols. It is beyond the scope of the present course. But the ones which are commonly used have been discussed in the lecture series.

We have talked about Sol-gel techniques, the hydrothermal techniques, the sonochemical techniques, the mechanical milling techniques and as we move on you will see we will talk about lithography and to an extent about laser ablation techniques which are used to make the useful materials. By tuning these synthesis protocols, what are we trying to obtain or manipulate? We are trying to obtain new morphologies because of which we can tune the surface area of the particles. As the surface changes, the packing densities would change and the nature in which these particles would change. their shape would decide the porosity of the materials and then you will have different channel structures which would get stabilized and that would facilitate different nature of electrolyte intercalation leading to modified ion intercalation or deintercalation. And finally, you can also modify the particle size of the system and you can go from bulk to nano and you already understand what are the major impacts if we tune the particle size of a material.

So there are various ways by which you can have different types of electrode materials which are being used in supercapacitors. In EDLCs, these are the typical carbon structures which are being utilized. For example, if you see the scanning electron microscopes or the transmission electron microscopes, you can see the scales. You can see that they are much larger and these are activated carbons. You can go to much smaller size particles.

These are carbon microspheres. You can go to even smaller carbon structures. So, you can see there are very small particles of carbon and the size is less than 100 nanometers or so and they are called as carbon nanospheres. You can have layered structures like graphitic or graphene oxide or reduced graphene oxide. And finally, if you go to confinement in all

the three directions that means you go to a quantum dot structure, this is a typical TEM of a graphene quantum dot-based system.

So, you can clearly see that if you compare the morphologies and shapes and sizes of these carbon structures, they are clearly different. No question about that. And therefore, what will be the consequence? The consequence would be straight away that the storage capacities of the systems would be different because of the different nature of electrostatic layers which would stabilize near the electrode electrolyte interface. So, clearly change the structure, change the morphology you will get different capacities. As we had seen from the SEM micrographs the same can be corroborated using the BET surface area measurement.

So, you determine the specific surface area of these particles. For example, activated carbon have surface area of approximately 930 m^2 per gram. Carbon microspheres can have much lower values. and then other systems can be in between. So, you know that as you move from one system to the other, if the surface area is different, then the reaction kinetics are quite different.

Why? Because surface area will define the number of particles which will be on the surface of the system or they would be covered within the bulk and they will not take part in the storage mechanism. So, you can play with the surface area and modify the storage capacities of these particles. If you find out their pore size distribution, what is the typical pores which are there in these systems. These are required because that would facilitate the incoming electrolytes to enter certain part of the electrode film and then they would have interaction with much higher number of particles. So, you have clearly modification in the pore structures also.

What is the typical importance of these pore size distribution or pore structures? A more porous nature increases the surface area of the materials. Because if two particles are coalescing, that means you don't have any ability to intercalate in the middle. But if you have two particles which are separated by a pore in the middle, there is a void and gap in the middle, that means you have all the area which is accessible for the electrochemical reactions to take place or the charges to form. around the particles. Therefore, a more porous nature of the material increases surface area and hence it has direct impact on the electrochemical performance of these materials.

And the field of porous materials for energy storage devices is becoming very important in today's world. So, this is what we said if you have the pore structure then the charge storage would be much higher and improved if all the systems for examples these particles are coalescing then you would not be able to access the inner sides of these particles and you will lose the capacity to have the electrostatic layers which are forming and therefore the storage capacities would be much lower. These are typical morphologies which are

being used for pseudocapacitive materials. Those were carbons. Now let us see the morphologies which are used for pseudocapacitive materials.

You can make different kind of materials. You can have for example nickel cobalt oxide. You can have nickel manganese phosphates. You can have chromium oxides, cobalt oxides.

You can have copper oxide. It is clear that the morphologies are very different. You can go from a solid sphere to a rose-like to a cactus-like particle to a pillar-like morphologies or sheet-like morphologies. You can now just imagine if you are having an electrolyte that is a aqueous electrolyte. So, now these electrolytes have to access different particles, so that there could be redox reactions taking place. Obviously, the nature in which the electrolyte would diffuse inside these particles or the ensemble of particles.

Then would be very different. And what would be the result? The result would be that the electrochemical performance would be very very different. The consequence is that the modern-day research is moving towards the development of smart functional materials with different types of morphologies ranging from one-dimensional to three-dimensional confinement and then modifying the electrochemical response characteristics. If you see one of the major research areas nowadays is in the field of hollow structures. We have been focusing on these structures.

For various applications. So they are being extensively used in today's world and they are considered as one of the future materials which would become very useful. Let us take some examples to explain these concepts even further. Iron oxide. Ok. So, you synthesize these materials, you can synthesize either porous structures or you can even have hollow structures.

These are the two protocols which are used to synthesize the porous rod like structure or hollow spheres. morphology change does not mean that the crystal structure or the lattice of the system is changing. It is only the shape of the particles which you are seeing are changing. The building blocks that is the unit cell remains the same.

So, Fe_2O_3 remains as Fe_2O_3 . It does not mean that if you go from a porous structure to a hollow structure that means you are changing the crystal structure of that. It is only the particle shape and size which is changing, not the unit cell. That is one thing which you should understand clearly. So, you can then carry out the X-ray diffraction studies, index the peaks and you will find that both the particles have exactly the same diffraction pattern as that expected from iron oxide and hence you confirm that you have formed iron oxide but when you take the SEM pictures you will see that their shapes would be different. What would be next? Next would be determining their specific surface area.

So if you have the adsorption desorption curves that is the BET adsorption desorption curves you will see that the typical surface areas which you are calculating would vary and for a porous electron you have a typical value of around 60 plus minus m^2/gm . Now, you can make various types of structures by changing the synthesis conditions. So, you can tune the porosity on the structures which are there. So, you can clearly see the porosities on the structures are different. So, you have these materials where the surface is much smoother than another material where it is much more porous and then you have the hollow particles.

This is a typical TEM. The change in the intensity clearly shows that the particles are forming at the edges and you don't have any structures forming in the middle. So, what do you get? You get the average diameter of these particles are around 90 nanometers for hollow structures and the dimensions for R1, R2 and PR2 systems are in the range of 10 micrometers, 4 micrometers to 450 nanometers. So, you are going from bulk to towards higher degree of confined based materials. Another technique which is used to understand the chemical composition and oxidation states. As you know, iron you can have in +3, +2 and +4 state.

So, which of these states are getting stabilized? So, you carry out the XPS studies and you will find that these materials are stabilizing in +3 oxidation state. After you have confirmed that these materials have stabilized, they are in single phase, you have a solid solution leading to Fe_2O_3 , you will find that the materials can be used for electrochemical analysis. As we discussed in the previous class, we will start with the three-electrode assembly having a reference electrode, a counter electrode and you have an electrolyte, an aqueous electrolyte and then perform the CV, CD and electrochemical impedance studies for ensuring that the device is useful for industrial usage, you have to ensure cycling stability. That means a typical supercapacitor is expected to be stable for 100,000 cycles. So, you must do cycling studies and see that its performance remains stable and it does not degrade very fast.

Otherwise, there is no use of making these devices. Let us see how you will make these materials. these are the powders so what you will do you will mix the powders make a slurry out of it and after you have obtained the slurry you will actually use a spin quarter to quote these powders or slurries on a substrate which will act as an electrode surface and that would be used to characterize the performance of the material. So, you can see that in this video. Then comes the details of three electrode measurement techniques. So, you will have counter electrode, the reference electrode and the working electrode.

They have to be arranged, connected to the potentiostat, galvanostat which will give the signal and then analyze the output signal and the video shows you how this is going to work. So you can have a look at the video and the video is self-explanatory. Once you carry out these analysis, what you will see? You will find that using these cyclic voltammetric

measurements, the CV curves without even going in detail, just by looking at the IV curves, you can clearly see that the storage capacities are quite different. Because the area under the curve which is the storage capacity is very different in these materials. So, there is no question about it that you can see different areas under the curve.

So, if you plot these specific capacities. As a function of scan rate, at what rate your system is being scanned, you will find that the values can change significantly in all the materials. So, typically you can have as high as 53 farads per gram at 50 millivolt per second scan rate. Along with that, you can see there is a prominent redox peak which is appearing in the CV curve so you know that there is some redox action taking place which means at this voltage the system is actually taking electrons and therefore you are having lower current and in the original cycle it will be releasing the electrons and you will have the corresponding reaction. If you do the same studies for charge discharge, you can clearly see these are the typical CD curves for the three materials. From here also, you will find that you can reach very high capacitance values, something like 82 farads per gram.

Please remember, we are comparing with conventional capacitors which have the capacitance values in the range of millifarads to microfarads. Here you are talking in terms of 100 plus minus farads per gram, per gram because we want to normalize with respect to the weight of the active material which is being used and therefore, we are calling it as specific capacitance. So, you can clearly see that you have nearly six orders higher value in specific capacitance in comparison to the conventional capacitors. As I said, you must carry out the efficiency test and that is the ratio of the discharging time upon the charging time because it will give you the magnitude of charge which is actually delivered by the device with respect to the charge which was fed into the device and it is the useful charge that is the one which is obtained during the discharging of the cycle which is more important. So, ideally η should be nearer to 1, but you will find it can be slightly less.

So, then if you have a structure which is being formed, then you draw the equivalent series resistance and then you will get from equivalent series circuits how the layers are forming, how the charges are getting formed. You can calculate the typical internal resistances of the materials. Finally, what you should see? You should see that how stable they are as a function of cycling. So just to show a typical value of up to 1200 cycles also, I've used this data, you will find that the performance is nearly stable for all types of materials and the morphology of the particle also does not change after thousand cycles or more. This means the material is stable, it is giving you very high capacitance value and therefore it is extremely useful for the field of supercapacitors.

I hope now it is clear to you that there are various types of electrode materials that are useful for supercapacitors. You can make new types of devices. Any new device can be fabricated other than the one which is already available in the market. How will you make it? Just choose a new material, tune its morphology. that will lead to the modification in

surface area and the pore size distribution which will directly impact the electrochemical performance of the device.

So, you can easily make a new supercapacitor which can store large amount of energy and deliver them as per the requirement of the end user. you can make either EDLCs, pseudocapacitors or you can also make hybrid capacitors which are a combination of EDLCs and pseudocapacitors. To develop more understanding about this field, you can look into these references and I thank you once again for attending this lecture of week 10.