

Physics of Functional Materials and Devices
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Lecture 39, Week 10

Introduction to energy storage devices and basics of supercapacitors

Welcome again. In this week, we are talking about the application of functional materials in various functional devices. In the previous two lectures, I had talked to you about the use of functional materials in sensors. Let us move our attention to another area which is very important these days that is the field of energy both in terms of generation and storage. So, how the functional materials which we have discussed in this course have become an intrinsic component for technologies both energy generation and storage. In this lecture, let me introduce to you the concept of energy storage, the requirement for energy storage and what are the various energy storage technologies that are being proposed or investigated to make the future renewable energy-based landscape a secure and sustainable architecture.

To start we will discuss on capacitors, those are conventional capacitors, how energy is stored in these capacitors. why is there the need to move from conventional capacitors to another technology which is nowadays being called as super capacitors and the use of functional materials in such super capacitors would be discussed in today's class. What is the meaning of energy storage? as the very word suggest you have energy which is being generated. Before it goes to the end user you want to store that energy somewhere and then only supply it to the end user.

So, there is a component in between the generation unit and the user. It is also important to understand why these storage devices or systems are so important for renewable energy-based landscape. Now, for example, let us talk about solar energy. What is happening in solar energy? You have solar light falling on the photovoltaic cell and leading to the generation of electricity. Very simple, but I add another question to it.

Is the generation same during the daytime and night? or is the generation or efficiency of the solar cell similar during a bright sunny day and a cloudy overcast day or as you move from one season of the year to the other that means, the angle at which the sun rays are hitting a place is changing, you go from winter to summers and then you have monsoon in India. Will the efficiency remain the same? No, that means, these energy storage technologies which are based on solar will have intermittent nature. Sometimes they would be working extremely well and then there would be time where their production would be

quite low and the property of this is intrinsic you cannot change it. So, the intermittent nature is intrinsic to solar based generation unit. Similarly, if you talk in terms of wind, the you will find that there are days where the wind velocity is appreciable.

So, that it can drive the blades of the wind turbines and there are days where the wind velocities are quite low and they do not have the energy to drive the turbine blades and therefore, the blades cannot extract power from wind which can then be converted to an electrical signal and sent for usage by the end user. So, even wind has intermittent characteristic. So, you will find that renewable based energy systems have intermittent character. Along with that you will find that the usage of energy is also not constant, but vary during the day time. So, if you have a winter day and it is bright sunny outside.

What will happen? You will require large amount of electricity let us say at around 12 in the night that is 0 hours, then you go to around 1 am, then 2 your it is still cold and you are using lot of electricity because the heating systems are being used, but many of the shops and markets are closed. So, your usage and requirement for electricity is actually reduced. becoming nearly compensated and you can maintain the supply. But at 8 o'clock in the morning where all the offices start to open and you have these offices being heated, you are still using lot of electricity at homes for heating water, for heating the rooms, the schools are open. shops are going to open there is a certain surge of electricity.

Then at around 1 o'clock daytime the sun is shining the temperature increases then you have seen that most of us will switch off our heaters at home and you would like to be in sun. Ok, Now, the industry is working the shops are there which are open, but the requirement for heating is coming down during winter. this time of 12 to 3 in the afternoon. So, your requirement for electricity comes down. So, there is fluctuation in demand, but if you compare the performance of a solar cell during this period of 12 to 3, the sun is just overhead shining brightly on the solar cells.

So, your efficiencies are highest during this time, but the requirement has come down. So, what has happened? This is again a mismatch in requirement and supply. So, to compensate such fluctuations what you can do? When the demand is low generation is high you store the excess energy, but when the demand is high and source has limited efficiency that means, during night supply the energy which you had stored. along with that you can compensate the intrinsic character of intermittent nature of the generation unit. So, you can compensate the fluctuation in demand and also compensate and take care of the intermittent nature of the renewable sources.

Therefore, these energy storage technologies have become an integral component of all renewable energy base generation units. These units which are going to store energy would ensure continuity, restrict wastage. We will find application in mobile technologies, mobile just does not mean phones, it means your laptops, your phones, your smart watches, your

tabs. So, mobile technologies they are going to be used in e-vehicles. Along with ensuring the continuity and safety of the supply, they will ensure availability as per the need, they can be used for off grid application. So, if you are going to use it in villages which are not connected to your electrical grid, then you just have to have an off-grid system where you have local solar based generation units.

They will store electricity in batteries and from there they can power the households or shops or industries which are locally running in that region this will bring the balance between supply and demand. There are various types of energy storage devices mostly they are classified under four broad headings. These are under electrical energy storage devices or chemical energy storage devices thermal energy storage devices or mechanical energy type storage devices. The classification basically deals with the way this system store energy and in which form do they store energy. Let us start with electrical energy storage systems.

There are three most common technologies which you have read and you have heard or may have heard about. These are batteries, capacitors and super capacitors. They vary from one another by the way they store charges, their energy densities, their power densities, their cycling life, their cost and the materials which are used to fabricate these. Before we start talking about these technologies in details, you must know that there are certain terms which are associated with these technologies. These are capacity, energy density, power density and round-trip efficiency.

What is a capacity of an energy storage device? This is the amount of energy that is stored and the rate at which this energy can be delivered that is the power output. Energy density, generally you talk about energy. What do we mean by energy density? It is the amount of energy stored per unit mass or per unit volume. Similarly, you have power density, it is a measure of power output per unit volume or per unit mass. Per unit mass of what? Per unit mass can be of the active material which is being used to ensure that there is some charge storage or nowadays it is also in terms of the mass of the final device.

So, it can vary, but the normalizing term is per unit mass. Finally, you have round trip efficiencies. This is the amount of energy that could be extracted in comparison to the energy that is being put in the energy storage device. What is a capacitor? A capacitor is an electrical element which stores charges that are generated on two oppositely charged plates. This is what we know and these charge plates are separated by a distance and there is a dielectric in the middle.

So, if you have the conductors, the metal plates or the electrical conducting plates parallel, they are separated by a distance d and you find Q is the charge which moves from one conductor to the other. What would be the voltage that would get generated? Obviously, that would be proportional to the value of Q . If you define the capacitance as the

proportionality constant, then you will find that it relates the value of V and Q. We have heard and we know that there are different types of conventional capacitors. You have paper capacitors, ceramic capacitors, film capacitors, electrolytic capacitors, glass capacitors, polymeric capacitors.

If you have these capacitors, they are they can be if you want to have higher storage capacity you can add them in series or parallel combinations. So, if you have parallel combination of capacitors, you will find that $Q = C_{ab} * V$. So, you have the total ability to store charges and $C_{ab} = C_1 + C_2 + C_3$ and so forth. But in if you have series combination you have the value of V which is given by Q / C_{ab} and you have $1 / C_s$ which is the capacitance given by $1 / C_1 + 1 / C_2 + 1 / C_3$. So, what would be the energy density? If you have the charges that is on one side you have + q on the other side you have - q.

For example, at a given time you have q charge small q which is a function of t which is getting stored. What would be the instantaneous potential that would be q / C? Total work which you would be doing to take the system from 0 to Q would be equal to $\int_0^Q 1 / C q dq$ 0 to q integration that is equal to $q^2 / 2C$. So, work done dw would become equal to $\phi dq = q / C dq$ Let the final potential difference be V. Therefore, $W = CV^2 / 2C = (1/2) C V^2$. This is the total work done and is stored as potential energy in the capacitors.

We have seen that you have parallel plate or you can have series combination of capacitors. Now, if you have parallel plate capacitor that means, you have the two conducting plates separated by a distance d and a dielectric in the middle what is the capacitance? A capacitance of a parallel plate is proportional to the area of the conducting plates. So, area of the plates and inversely proportional to the distance between the parallel plates. To improve this value either you will have to increase the area or decrease the value of d or you can introduce a dielectric constant which is then going to modify the formula to $C = K \epsilon_0 A / d$ and if you introduce a dielectric constant of higher values then also you can change the value of C. But the increase in the capacitance value is not to an extent where we start saying there is a dramatic change.

So, you can have μF , mF kind of capacitors. But, as we move towards miniaturization, as we go for higher storage in lower or smaller areas, it was felt that you need to have new storage mechanism and that is where the concept of supercapacitors came into picture. These are slightly different from conventional capacitors. They can store extremely high amount of energy and then discharge them at rates demanded specifically by the end user and the capacitance values which we are talking about are not like microfarad millifarads, we are talking in terms of few farads to hundreds of farads. So, you have 1000- or 10000-times higher capacitance values which can be obtained.

So, if you have very high values of C that can be obtained. This means you can reduce the area to obtain similar capacitance if you were talking in terms of conventional capacitors.

So, you can reduce the area without having the requirement that you have to bring the two parallel plates very near to each other and that brought a massive improvement in the storage capacity of the capacitor technology. Based on these storage mechanisms, these capacitors are mostly classified under three types. The electric double layer capacitors.

The pseudo capacitors or hybrid capacitors. You will find all these mechanisms or classifications are based on the materials properties and the way the material stores charge. Now, the moment I start writing you will find that the word material starts getting repeated. In conventional capacitors it was just the parallel plate capacitors, but here you have the concept of materials. what it tells you immediately? It immediately tells you if you make new types of material you will be able to get new supercapacitors.

If you have new supercapacitors you can play with the storage capacities that means, you are going to have different values of $\frac{1}{2} CV^2$ because if you have material which can remain stable or have an operating voltage window of around 2 volts, then you will have V^2 that is $\frac{1}{2} CV^2$. So, you can go up to 2W of power. or you can go up to let us say 2 W hour energy that is can be stored by these kinds of capacitors. So, you are talking about large change in these systems and you can then make new materials. Let us see what these materials have to go through before they can become useful for such devices.

The first measurement these materials have to go through is the cyclic voltammetry as we had seen in the previous lecture. It is basically current versus potential curve; you have the forward cycle and you have the reverse cycle. And then from the nature of this curve you can find out the information about the potential window in which the material is going to be stable. what is the typical current up to which they are stable and there is no evolution of hydrogen or oxygen if you are talking in terms of electrolyte solutions which are based in water. How reversible the systems are that means, the nature of the curves do not change for how many cycles and you can also talk in terms of continuity of the overall process.

Then you have the constant current that is the galvanostatic measurement from there you can find out information about capacity, reversibility, resistance that is internal resistance and the rate of diffusion. This method is of two types you can have cutoff voltage control or constant capacity cutoff control. So, you can have in the cutoff voltage control that is called the charge discharge measurements. Here you can then plot dQ/dV against voltage based on time and voltage values and from there you can determine the value of capacities. Let us see how you determine the value of capacitance from the C-V profiles that is the I-V curves.

Capacitance we know is equal to dq/dv . Current flowing through the circuit is dq/dt . Combining these two equations what you will get? C is equal to $\int I dt/dv$ where v is the voltage window. Scan rate is defined as dv/dt So, you can combine the above equations

to get that $C = 1/v_s \int_{-V}^{+V} I(v)dv$ If you divide by mass then you get the specific capacitance. C would then become $1/mv_s \int_{-V}^{+V} I(V)dv$ So, this is a simple formula of determining the capacitance from the I-V curve. So, you know what is the voltage window, what is the minimum voltage to maximum voltage with to which you are cycling the system, you know the current which you are obtaining at different points and then you integrate in the two range and you will be able to get the value of capacitance.

Similarly, from CD if you have the charging time and the discharging time cycle. So, this is the charging time and this is the discharging time curve, then see again dq / dv , $I = dq / dt$. You can write dq as integral of $I dt$ total charge that would get accumulated at the electrode would be $dQ = I\Delta t$ voltage developed at the electrode which is excluding the voltage drop that is the internal drop in the device. So, you can have ideally you want a triangular shape, but what you can get is something like this. So, here you have an internal drop coming in because of the internal resistance.

So, you will have dV would be equal to $V - IR$ that is the internal resistance. if you combine this information and divide C/m you will get C_s that is the specific capacitance is equal to $I / M * dt / V - IR$. So, now, you can easily find out the storage capacity of a material. Please remember that you use the discharging cycle to determine the storage capacity of a material. Why? Because that is the useful storage capacity.

Because suppose you have x amount of storage while charging, but what is useful to you? How much the material returns back? If it consumes 50 % then you are losing 50 % of charge. So, that is getting lost in each cycle. So, you are losing lot of energy. So, what is a useful storage capacity is determined from the discharge cycle of the material and that is where your Coulombic efficiency comes into picture or the round-trip efficiency comes into picture. So, what would be the efficiency? The amount of charge which is being obtained after discharging divided by the total charge which went in during the charging cycle.

The nearer they are to 1, the higher is the efficiency and better is your system. So, as we said you have materials which will drive the performance of such storage devices. And you will find that nanotechnology is playing a critical role in the advancement of these technologies. So, you can have different types of materials 0D, 1D, 2D, 3D types of materials. You can have different morphologies of these materials and based on that you can clearly see that the surface areas are changing.

If that is happening the interaction at the surface would change and therefore, the redox activities that is the giving of electron or taking of electron will change and your storage capacities would change. You have seen this curve you can go from bulk material to a quantum dot-based structure. Before the use of these materials in storage devices, the synthesis of these materials it is important to characterize these materials and then only we

can propose the use of these materials in the storage devices. This we will discuss in the next lecture. So, in today's lecture I hope it is clear that energy storage systems and technologies are very important and will remain an integral component for renewable based generation units.

There are various types of energy storage systems classified under four broad headings and we have introduced to you the concepts of capacitors, and super capacitors. In the next lecture, I will discuss super capacitors more in details and you will find the use of functional materials in such super capacitors. You can read these references for developing further understanding in these areas and I thank you for attending lecture number 2 of week 10. Thank you very much.