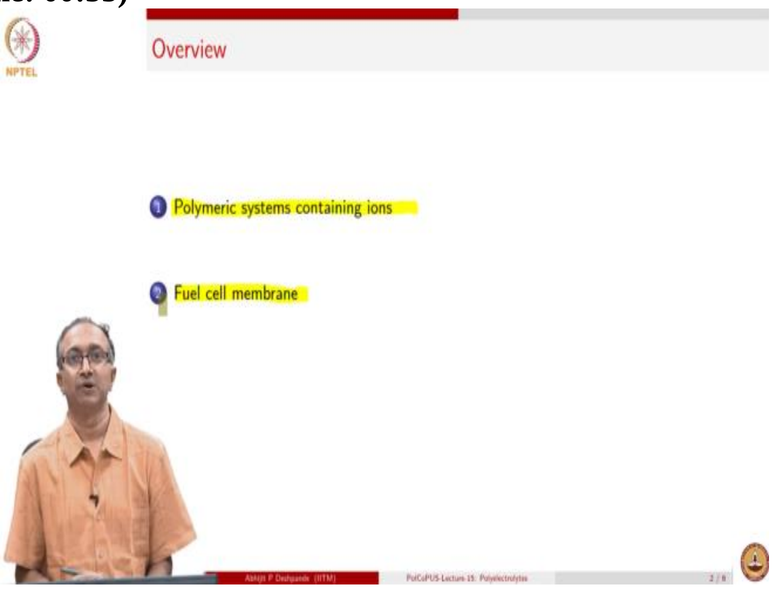
Simple Concepts Related to Single Macromolecule
Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology - Madras

Lecture - 15
Polyelectrolytes

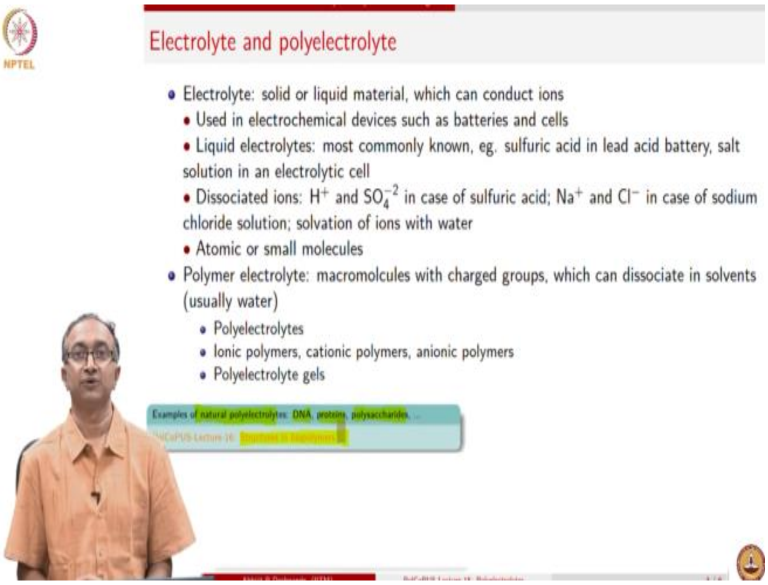
Hello, let us continue our discussion of polymeric materials. In this week, we are looking at properties of a single macromolecule. And we have already seen example of how a single macro molecule size and its flexibility and its shape can give us very good insights about even the bulk behavior. One important aspect of single macromolecule is the charges on it. And we have already discussed polyelectrolytes - polymer and electrolytes. And so, in this lecture, we will look at polyelectrolyes from the applications point of view.

(Refer Slide Time: 00:55)



And we will do this by first looking at several examples of polymeric systems which contain ions and then we will pick up 1 specific example, many of you may be familiar with fuel cell, we will look at example of a fuel cell membrane where proton conduction is done, which is an electrolytic activity using the polymeric membrane.

(Refer Slide Time: 01:22)



So, looking at what is an electrolyte? Electrolyte is a system which can conduct ions and we know that electrolytes are used in cells and batteries. Cells and batteries are combination of electrodes and electrolytes. Electrodes is where conversion between electrons and ions happens or electro chemical reactions take place and electrolyte is the communicating channel between the 2 electrodes the cathode and anode.

So, therefore, electrolytes are generally liquid materials. We are quite used to examples such as sulfuric acid in lead acid battery, or of course, we know that any salt solution is also an ionically conducting medium. So, all these can be used liquid like systems can be used as electrolytes. Electrolytes can also be solid ionic conductors, we have ceramic solid ionic conductors we have systems where the state is solid, but ions can conduct.

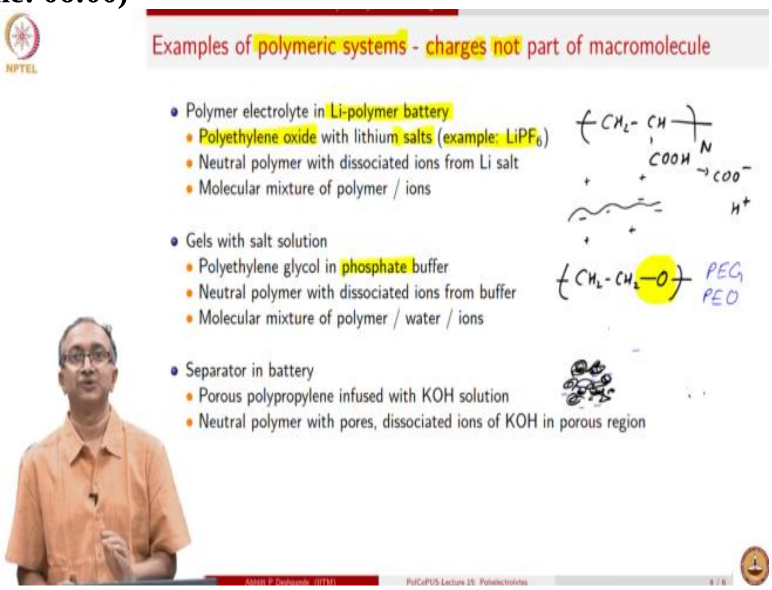
So, in all of these liquid or solid system, ions presence and dissociated ions presence is required. These are the ones which can diffuse or migrate or conduct. And in case of most of the electrolytes that we know they are either atomic systems or molecular systems. In case of polymers, what we are looking at is macromolecules with charged groups or ionic groups and these ionic groups can dissociate once a suitable solvent is present. Here, I just wanted you to look at the term polarity of a solvent. Later on, when we discuss about suitability of a solvent for a polymer, whether a polymer dissolves in a solvent or not? And how the interactions are between solvent and the polymer? This term polarity will be quite useful. So, generally polar solvents are required for dissociation of ions.

So, water is the most common solvent that we know, but it need not be water alone, there are other solvents and I want you to go and look up some of these. And, these are some examples of other polar solvents and what is meant by polarity? And clearly that will indicate presence of dipoles. So, and if polymeric systems macromolecules also contain certain groups, which can interact with solvent then interactions is possible in case of polyelectrolyes there are ionic species present and they clearly will interact with polar polar solvents.

So, general terms which are used to describe these polymers with electrolytic properties are polyelectrolyes polymer which are electrolytes, we also use polymers which contain ionic groups therefore, ionic polymers and of course, since we have positive or negative ions, we can have cationic polymers or anionic polymers. And we have anionic polymers and cationic polymers as very useful in water treatment or or in separation of molecules, many of these ion exchange resins we have these depending on what is the ion that is the target. Sometimes we also will refer to them as gels meaning that they have solid like properties, but they contain a lot of water usually in them. So, we also have of course, large examples of natural polyelectrolytes, in fact, biology is full of examples where ionic interactions are very crucial to the function of the macromolecules.

And so, whether it is nucleic acids or proteins or whether pectins or other examples of polysaccharides they all are, they all contain ionic groups, and they are all polyelectrolytes. So, we will spend some time in the lecture on structure of biopolymers looking at some of these polyelectrolyes which are natural.

(Refer Slide Time: 06:00)



Now, even though polyelectrolye is a generic term and sometimes it is used for those polymers, which actually along the chain do not contain an ion. So, this example I have given earlier also where we looked at polyacrylic acid. So, if you recall, if we were to draw this as a chain then we can say and there are many places where this -COO group is there and this can dissociate into -COO and H+. So, I will drop polyacrylic acid by indicating that there are a lot of dissociated COOH groups.

So, this is how macromolecule itself contains ions, but we have several examples of polymeric systems where charges are not part of the macromolecule and 1 example of that is lithium polymer battery, which is by the way the most common example of an application of a polymer electrolyte in a battery in a practical application. And here the polymer is polyethylene oxide, which is nothing but as the name suggests ethylene oxide repeating units so, you can see there is no ionic group along this chain.

So, how is it that this can be an electrolyte? This becomes electrolyte because we actually add a salt along with this polymer and this salt can dissociate and then, you can have these lithium ions conducting and why is polyethylene oxide used along with this lithium salt? What is so specific to polyethylene oxide that makes it suitable to be used with these lithium based salts? So, lithium based salts are required from a lithium battery point of view. So, we already know lithium battery is quite commonly used and earlier lithium ion batteries contain inorganic electrolytes.

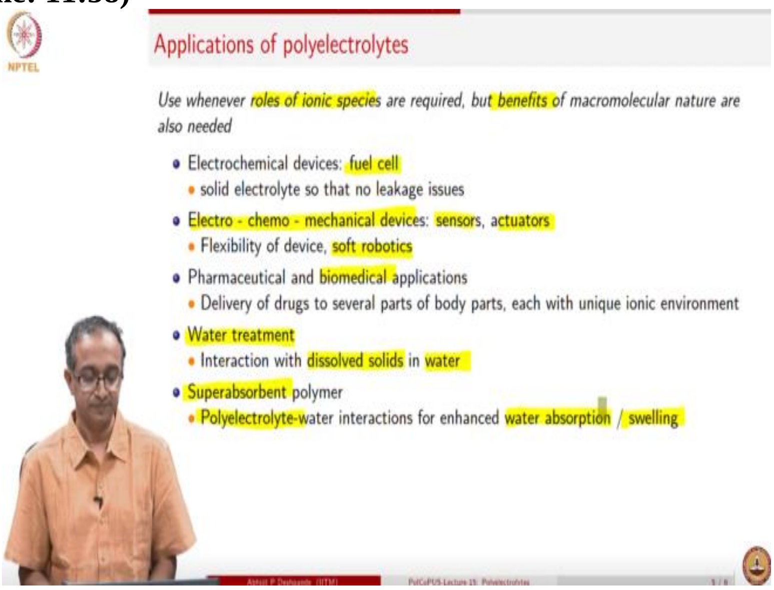
So, when we are trying to replace it with a polymer electrolyte clearly we know that lithium ions will be required. Now, what is specific about polyethylene oxide that makes it suitable and here the crucial aspect is this oxygen group and interaction with lithium. So, in fact, if you look at polyethylene oxide, what you have is the chains of polyethylene oxide which contain all these oxygen along the chain and the lithium ion actually interacts with these. So, in fact polyethylene network polyethylene oxide network is like a mesh in which these lithium ions are getting tossed around.

And so, the conductivity in such a network where because of the movement of the macromolecular segment, lithium ion also gets starts hopping around from one place to the other, the conductivity is high. So, that is the basis for using polyethylene oxide, though it does not have an ion itself in a lithium ion battery, we similarly have examples of materials where we will use PEG, and just to remind you that PEG and PEO are one and the same thing polyethylene glycol or polyethylene oxide. So, the same molecule is also used by making a gel out of it and in which case there is a lot of water because, again the same role of oxygen, where we have these polymer chains and they may be cross linked physically or chemically and then there is a lot of water present 70, 80% 90% water present and this water is added with ionic species.

So, this is like a sponge like material in which water is contained, there is 1 small way in which analogy of sponge and this is misplaced. In this case the mixture of polymer and phosphate buffer is molecular everywhere molecular mixing is there between the solvent and ions and the polymer chain. However, polymers themselves do not contain the ionic groups, one the last example is where the sponge like analogy is completely valid and that is the case of porous ion. So, in this case what we have is pores of , polypropylene which is a hydrophobic polymer and but which has porous so, in the pores, there are KOH solution.

So, this is an analogy where sponge is there and wherever there are pores of the sponge there is KOH solution filled and in this case, the polymer is acting completely only to give mechanical rigidity to the system. Otherwise, the whole role is played only by the potassium hydroxide solution. So, we have seen some examples. So, sometimes people may refer to these things as polyelectrolye, but they are not they are not macromolecules which contain ionic groups. These are polymers which do play a role of electrolyte in a either cell or battery system.

(Refer Slide Time: 11:58)



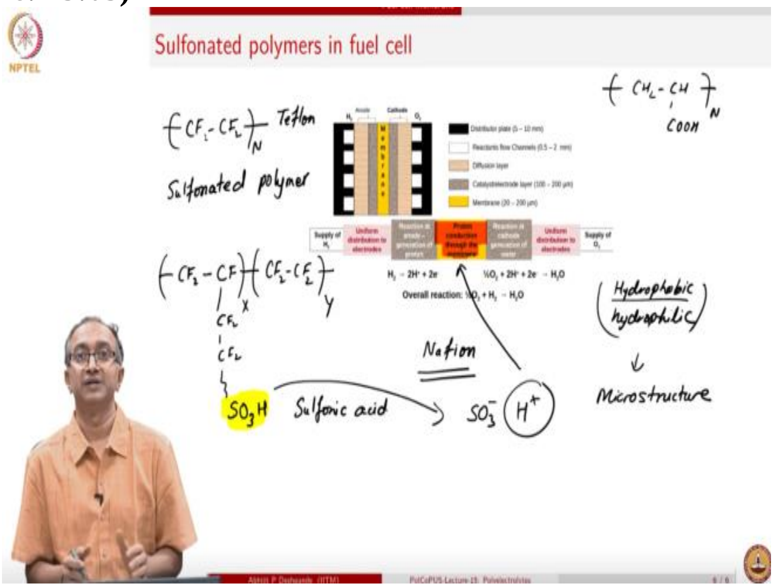
Looking at where are all the places where polyelectrolyes are used. We will use poly electrolytic systems or macromolecular systems which have ionic groups along them wherever we need ionic species, but we need benefits of macromolecules. So, what are these benefits? We need ionic species conduction, but at the same time we need benefits and these benefits could be in terms of solid like systems as I have already mentioned so, no leakage and a variety of issues which are associated with liquid systems, corrosion.

So, many of these things could be prevented if we use a solid like material, but with a macromolecular system we could bring in additional benefits in terms of flexibility in terms of easy shapes that can be fabricated and so on. So, any benefit that we have discussed so, far with polymeric systems. And the examples here are plenty fuel cell we use the ionic polymer or a polyelectrolye, there are lots of examples in robotics. So, sensors, actuators not just in robotics, but various other application wherever we need electro-chemo-mechanical, this is a very interesting term we have electrical response which means conduction is involved conduction of ions, electrons possibly and we have chemo because we may change the pH we may change the salt environment, we may change the temperature and pressure and so on. And then mechanical because there is deformation involved.

So, because of deformation electrical or physico-chemical properties may change or because of electrical or physico-chemical properties changing mechanical response will be there. So, these are nothing but sensors and actuators just like in our body, because of biochemical reactions, we can get either sensing or acting can happen actuation can happen. And of course, pharmaceutical and biomedical applications are important wherever drug delivery to a specific ionic environment is needed. Water Treatment is an extremely important area of poly electrolytic usage, because dissolved solids and many other salts which are there in water can interact with these polymeric systems and polymeric system can play a role of making an agglomerate of the dissolved solids by interacting with all these isolated salts and therefore, leading to an effective separation of dissolved solids from water.

And one very common example is also related to diapers, sanitary napkins and other health related product where absorption of aqueous fluids is required. And in this case, if we use a polymer, which has ionic groups then the amount of water that can be absorbed is extremely high. So polysodiumacrylate for example, which is used in many of these applications, it can absorb up to 8 times its own weight in terms of the water. So, very high degree of swelling and water absorption is possible.

(Refer Slide Time: 15:03)



So let us finish this lecture by looking at this example of fuel cell. So, I have just put this graph of the graphic of fuel cell, you can just do some search and try to read more about it, I will only focus on the polyelectrolyte part, which is serving as a proton conducting medium. And once we say proton conduction is needed, of course, we know sulfuric acid or any other acid can be used.

So, the key here is to get a polymer which has acid and immediate response given so many times we have discussed maybe that you know, why do not we use polyacrylicacid. So, this definitely can be used as an electrolyte, but the problem with this is as soon as you add it with water, it will dissolve. So, some of the systems which some of the issues which are there with liquid electrolytes will also be present with this. So we need a mechanically robust polymer, but at the same time, it should have acidic groups which can conduct ions. And so, one of the most stable polymers, if I ask you, what comes to your mind? What will it be very stable polymer? And if you look at it from the point of view of wherever there is corrosion problems, wherever there is a lubrication required, wherever there is very good, kept physic-chemical stability required.

In fact, in kitchen when we use nonstick, where high temperatures and oil and water and different types of substances are involved. Yes, I am sure many of you have arrived at the answer the Teflon. So, Teflon is an example of a very robust polymer and it is a fluorinated polymer and so, this can be used in an electrolytic setting. So, it will be resistant to oxidation, reduction and any other complications that are available in a fuel cell or a battery. But the problem is it does not have any ionic groups for conduction. So, variety of fluorinated ionic polymers are there and all of these are called sulfonated polymer, because on these Teflon backbone, what we have done is introduced is as an acidic group.

So, if you have a chain and at the end you introduce, what is called a sulphonic acid group? So, you can have a group like this and you can also have the Teflon backbone. So, what I have drawn here are several examples, but the most common one is Nafion whenever we talk of ionic polymers and its applications in variety of fuel cell situations, but also in terms of sensors, actuators, wherever there is proton conduction required, this is an extremely important polymer and many new materials which are being tried to be developed over the last 20 years, the target is to say, can we get as good a performance as Nafion and that is because, we have this fluorinated backbone, because of which the dissociation of this is extremely efficient.

So, we get proton which can then conduct and so, this is a fascinating example. Nafion is a fascinating example of where we have hydrophobic, hydrophilic part hydrophilic part is which is associated with this -SO3H group, hydrophobic part is the Teflon backbone and these are very interesting microstructure distribution. If you look at nanometer and micrometer size, description of this material, we will see that there are lots of islands and channels of the sulphonic acid groups and water.

So, with only 10 to 15% water, this polymer can conduct ions as good as a liquid sulfuric acid. And that is its advantage so, and conductivity is extremely high. But from all other points of view, it gives us a perfect benefit of a solid like material. There is something more to read about in terms in case you want to understand about how sulfonated polymers are very interesting from a polymers ions point of view.

So with this, we will close this lecture. Thank you.