[Scientific Innovation Series 5]
'배터리 기술의 미래' 녹취록

행사일: 2021 년 2 월 19 일

기록자: 박유원, 김지수

Introduction

현택환:

Good morning. Welcome to the Chey Institute Scientific Innovation Series. Today, as the fifth iteration of the series, we will focus on the future of battery technology and materials. I am Professor Taeghwan HYEON at Seoul National University. I'm very excited to moderate today's webinar with the world's leading scholars in the battery area. Before we begin, we will hear a welcoming remark from Chairman Chey Tae-won of the Chey Institute for Advanced Studies.

최태원:

Distinguished guests, Ladies and gentlemen. It is my great pleasure to welcome all of you to the Chey Institute's Scientific Innovation Series.

We wish to highlight battery technology as a key driver for future innovations, and explore challenges and opportunities facing us in this field. For today's webinar, I am excited to have four exceptional scientists. Especially, I have the great pleasure of welcoming Dr. Stanley Whittingham, won the Nobel Prize in Chemistry in 2019.

In science and technology, looking at the dynamics of past innovations is critical for refining new attempts to drive the industries of the future. The battery market owes its recent success in part to the long-standing collaboration among dedicated individuals in industry as well as academia.

We believe that collaboration will become essential to the expanding battery ecosystem, which includes developing new materials for next-generation batteries and recycling and reusing used batteries. For this reason, the skills to collaborate and communicate outside one's expertise are an increasingly important quality in future global leaders.

To conclude, I wish to express my genuine gratitude to our speakers, especially those joining from the US late in the evening.

Thank you.

현택환:

In today's conference, there will be four speakers. Two speakers, Professor Whittingham and Professor Ceder, will join us from the United States through Zoom and Professor Kisuk Kang and Professor Jang Wook Choi are here with us on site. In between, after two presentations by Professor Whittingham and Professor Ceder, we will have a 40-minute discussion session, and then Professor Kisuk Kang and Professor Jang Wook Choi will deliver their presentations.

Let me first start with the first presentation by Professor Whittingham. Let me introduce Professor Whittingham. He is currently the SUNY Distinguished Professor of Chemistry and Material Science and Engineering at the Binghamton campus. As you may know, he's a recipient of the 2019 Nobel Prize in Chemistry. He received his Bachelor’s and Ph.D. degrees in Chemistry from Oxford University. Now he is an honorary Fellow of the New College of Oxford University.

He is a true pioneer of lithium-ion battery. He started battery research in 1971, and at that time, he won the Young Author Award of the Electrochemical Society for his work on Beta Alumina. He worked on the intercalation chemistry, which actually led to the first commercialized lithium-ion rechargeable batteries made by Exxon. In 1988, he turned to academia, SUNY Binghamton, to initiate a program in Materials Chemistry. In 2018, he was elected as a member of the National Academy of Engineering. He received numerous awards, including the Turnbull Award from Materials Society of the United States.

Today, his title will be “The Lithium Battery, from a Dream to Readiness to Take on Climate Change – Opportunities and Challenges.” Professor Whittingham, please.

Plenary Session

Stanley Whittingham:

Thank you very much for that kind introduction. What I want to really talk about is where lithium batteries came from and where they're going to now and what they can do to help us all to get a cleaner environment. But first, let me say I'm part of the Northeast Center of Chemical and Energy Storage, and Gerbrand was also part of that for many years.

Most of my research is supported by the US Department of Energy, and I want to thank them for all that help over the last 30 years, but let me just show you what I plan to talk about today. I'm going to keep at least for half the slides, most of the science out of it and give more of a background. So, I want to start in about 1972 and come up to the present time because back in 72 we just had a, I would say, a semi wild idea and the interest then was electric vehicles—I’ll get into that in the moment—and then I'll talk about the cleaner environment and how batteries can help handle that, and obviously I can handle things like resilience as well to natural disasters. And this is particularly important in places like New York City where hurricanes come through, and California, where there's lots of fires and similarly in Australia. So, I'll also talk about what the limitations are and therefore what some of the scientific opportunities are for the scientists and engineers that I’ll finish off with a few comments about science is interdisciplinary and really knows no national boundaries, and we have to work across all these boundaries to be successful.

So, let me go back to the beginning and thank what was then, Esso. And you may know it now as Exxon or Exxon Mobil. Back in 1972, the company, they decided they were going to be an energy company, not just an oil company. And we started research on superconductors. Out of the superconductor research came batteries. They were large on fuel cells for a while. They were the largest manufacturers of solar photovoltaic cells in the United States. And they did all the nuclear reprocessing for the United States. So, they were a very large energy company. And their plan was for their research activity to be similar to the Bell Labs. So, let me just show you a few pictures here. On the right-hand side here is a paperweight that the company gave away to potential customers. And in this paperweight, what you'll see is a lithium-ion battery here, one of the very first ones ever made. And this was built about 1976. Next to that is a watch and then a small solar cell and this particular system is still on my desk today. This one was built about 1976. It still works very well. The weak link in it turns out to be the clock, not the battery or the solar cell. Beneath that is a large cell. This is six inches by four inches by about an inch thick. Exxon used this as an electric vehicle show in Chicago in 1977. This turned on and off a motorcycle headlamp all week long with no failures. So, Exxon was interested in electric vehicles at that time and in fact, had some extensive discussions in the late 70s, early 80s with Toyota about electric vehicles.

The materials we used are these large single crystals. And this is what we call titanium disulfide. I’ll get into that a bit later. And this is me a few decades ago. And you'll see men's clothing styles change with time. So, noting this little battery here if you want to see one of those. This is the battery. Same coin cell, little button cell. And 18 months ago, 15 months ago, Bob Hamlin, who ran the marketing and manufacturing at Exxon, and I looked in our basements and we found some of these old cells. And together we found an old brochure, this the marketing brochure. Exxon, that came out of a subsidiary called Exxon Enterprises. And these you now see in the Nobel Museum in Stockholm. So, again, these same cells, Glenn Amatucci at Rutgers tested these cells about three years ago and they still had more than 70 percent of their original capacity. So, lithium-ion cells are built very well. And I should say these are ceramic seals in them and welded close, so expensive cells, but they will last forever.

So, let's look at where we come from, from these small cells. And I'll show you a few examples here and maybe we talk about electric vehicles first. As said, we came from very small cells, which is really our dream, “Could we make lithium ion batteries?” to now the dominant. And now I show you three pictures of cars here. This is a small two-seater car that my wife and I drove in Bermuda on our fiftieth anniversary, almost two years ago now. And these were the first electric vehicles in Bermuda that had been there about two weeks. And tourists are not allowed to drive cars. And they passed a new law allowing them to drive electric cars. And we rapidly found out that range anxiety is real. So, you see, we're busy charging this one up. So, a small vehicle. On to the right here is two electric trucks. This is what we call a 16-wheeler, very large truck here, all the lithium-ion batteries. This is at eco research facilities about one hour north of Seattle in Washington. And their test track where they build these vehicles and test them. And on the right-hand side is a garbage truck. And this is almost ideal application for electric vehicle because they stop-start raise-lower all day long. So, I had the opportunity of driving both these around their test tracks. And it is extremely smooth driving. An example of another electric vehicle is this Mercedes EV bus. I picked this particular one because this as of, I think, maybe six months from now, will have the option for all solid-state battery. I'll get back into that little bit later. So, solid state batteries are coming in.

The real challenges of EVs is still range versus cost, and we have to address the issue of sustainability and recycling. If we look at energy storage, I think everybody knows the sun shines just the day if it comes out at all. And the wind only again blows intermittently. And in the United States, it tends to be windier at night when you don't need the power. So, we have to be able to store the energy. So, this gives us clean energy, which should help us in mitigating global warming, although some of us prefer to call this global messing up. And then you've been watching your televisions in the United States for the last two or three days. Places like Texas, Florida have had the coldest weather and snowiest weather on record. So most of the refineries in Texas are down now because they're not used to be covered in snow. Clearly, lithium batteries started out in communications and toys, and without lithium-ion batteries, we would not have our smartphones and our laptop computers.

Going to another extreme of lithium-ion batteries was where in Sweden 15 months ago two of the Physics Laureates and I had the opportunity of speaking live to the astronauts on the International Space Stations. And they were in the midst of replacing nickel metal hydride batteries with lithium-ion batteries. And they like the lithium-ion batteries because they are half the size, half the weight, and are going to last twice as long. And they are on the outside of the space station. So, the extremes of temperature, both hot and cold. So, the lady here is an American from the state of Maine, but her mother is Swedish. And the fellow is from Italy. And they were involved in installing these new batteries.

So, let me just make a statement for. really the politicians. If the virus has had one positive effect, it helped clean the environment. And about three or four weeks ago, the United States announced that CO2 production last year, that's 2020, was 10 percent less than the previous year. And I think it's critical that we take advantage of this and not go back to the old normal. So, I think we're going to have fewer meetings, more of us are going to work from home than drive to the office every day, and I think we're going to have more of these mixed Zoom and in-person meetings than we used to have. And basically, the battery is going to allow the world to move to an electrical society, both for generation and transportation. And we wrote an editorial that went in the French newspaper Le Monde in May last year, pleading with the politicians not to go back to the normal. I think the senior members of our field think we've done well in the battery area. It is now our duty really to help clean the environment, make it more sustainable and help mitigate global warming so our children and grandchildren can live in a cleaner environment.

So, let me just briefly say what role, really, of storage and renewable energy. Renewable energy, certainly in the States, is now cost effective. So, if we look at the State of Texas, and Texas is not exactly known as a green state, no subsidies at all there. As of last August, 94 percent of their planned new generation to go on the grid was renewable. And this is predominantly, as you can see on the right hand, solar, wind, combined storage, and a little bit of gas going on, essentially no coal, and nuclear is too expensive at the present time. I think grid operators are realizing there is minimal cost of operation for renewable energy. You need minimal staff and there's no fuel cost during operations. But it is intermittent, it needs storage. And storage can, in fact, eliminate the peaker power plants, particularly the dirty ones. And I show you an example of one here that went operational two months ago in December. And this is in Moss Landing in California about an hour and a bit south of San Francisco. This is a 1.2GWh facility. By far the largest in the world, I think three or four times the next largest, which is in San Diego, which is a bit bigger than the one in Australia.

This replaced a gas-fired system and the building you see here is where the gas-fired system used to be. And that's full of batteries as well as the ones on the outside. This is going to expand to one point six gigawatt hours in 2021, and they have approval to expand this to 6GWh. So, we're now talking about huge storage capabilities using lithium-ion batteries.

But before I get too far along, let me explain what a battery is and I'll go through this, as I gather maybe a large number of the audience don't really understand the batteries. So, any battery has three main components. The anode. That's one of the electrodes. And the cathode. And in between there's an electrolyte. And in a lithium battery, lithium ions pass from one electrode to the other through this electrolyte. So, if you look in here, the little green circles, they are the lithium ions. So, the key thing we did back in the 70s is look at how you could build a battery that would transport lithium ions and store electrical energy, as chemical energy was this lithium. And I already showed you a picture of titanium disulfide before. Let me go through a little bit of the history here. So, at Exxon, we started with pure lithium, then we went to alloy of lithium aluminum because pure lithium is not safe. It tends to form dendrites and short. Lithium aluminum works well for maybe a month or two, but again it eventually breaks down. So what Akira Yoshino did in Japan. He worked on polyacetylene and then found out that carbon materials would react with lithium well and you could store the energy there. And maybe I should briefly mention what this word intercalation means. If you look at an old dictionary, you'll find out that it describes intercalation as putting February the 29th into the calendar every fourth year and taking it back out again. So, it's a totally reversible event and that's how we use it in in chemistry. It means this reaction will go on forever, backwards and forwards. We do not change the structure of our materials.

I mentioned a little bit later, carbon is still what we use in batteries today, so carbons or graphitic carbons have been in use since 1990, so more than 30 years. The problem is they take up half the volume of the cell, so they have to be replaced. And we're looking at other materials to do that, such as tin or silicon. And a number of us are trying to go full circle and go back to pure lithium metal again.

The other electrode, so when this battery is fully charged, all lithium is on the left-hand side. As it discharges, the lithium goes to the right-hand side. So, I worked on this compound, lithium titanium disulfide, and I'll show you a picture in a moment. John Goodenough read our work and he was working at that time on lithium cobalt oxide and magnetic behavior. And he said, “This has the same structure, I'll test it.” The batteries, as we all know, worked exceptionally well. And it turns out this cobalt compound is still the one used today in your cell phones and in your laptops. There is a huge challenge with cobalt because it's very expensive and child labor issues in Congo where most of it comes from. So today, a lot of the cobalt is replaced by nickel manganese. So, this is what we mean by NMC. It means nickel, manganese, cobalt, still with oxygen. And Tesla and some other companies use nickel, cobalt, and aluminum. So those are two most common cathode materials used today.

John Goodenough also came up, some years later, with this compound called lithium ion phosphate. It is a naturally occurring mineral, and this has been used for energy storage and is used extensively in China, and I'll come back to that again because there are considerable advantages to it, but some disadvantages. And then I'll finish off talking a bit of chemistry about changing the iron and manganese from these phosphates with vanadium so we can put two lithium ions into the structure. And this will almost double our energy density. So, this is a big incentive for doing that. But let me go back and talk a little bit about titanium disulfide, why it was of interest. But before I do, let me point out in a battery, the lithium ion moves through the electrolyte, electrons move through an external circuit. That's where they do the work that drives your laptop or make your car go. So, we have to be able to move electrons in and out of these materials. So, the materials we use have to conduct electrons. And this was the big advantage of titanium disulfide, it has a metallic conductor. So, it conducts lithium ions and sodium ions and magnesium ions and I show you three examples here. So, this is behavior of lithium. This is the 76th cycle, this is run at room temperature and you can see these two curves are right on top of each other. The slight difference is due to the resistive losses and that electrolyte. Let me switch all the way to the right. And this is data that Linda Nazar got also on titanium disulfide, but now with magnesium. And this is in2018. So, you can see magnesium diffuses is very readily in this material. The same reason it's a conducting lattice and therefore there's no electrostatic repulsion between the lattice and the ions moving. The challenge with this big ion is, a highly charged ion is, it doesn't move very fast, so you have to heat the cell up and go a lower current density. But this is TiS, there is a record holder for magnesium cells at this time. It cycles very well, as you can see. In this little insert here, the red line shows the capacity here is very, very stable. In between, I show you the behavior of sodium. So, again, we can put almost any iron into titanium disulfide. You'll see this behavior here looks much more complicated. That’s because the sodium ion is larger. It forms a range of different structures, which means you have nucleated new compounds, and you get lots of voltage changes. So, sodium is much less attractive in the sulfides than lithium is.

So, let me now discuss—and don't worry about all the numbers on the slide. We get a lot of questions, “If you got the Nobel Prize, then surely isn't research finished? Everything's known?” The point we try to keep making is that today's batteries contain much less than 30 percent of their theoretical capacity. And in the circle here, I just show you the percentage of the theoretical capacity of five different cells, different chemistries. See, they vary from 11 percent to 20 percent. This is on a volumetric basis. There are about 25 percent on a weight basis. So, we still got huge opportunities to increase the energy density of the batteries, which means we can make them smaller and ideally lower cost.

Now, I’ll come back to how we're going to do that, but this is a United States Department of Energy project, where our goal is to get this number in this column up to five hundred. So, this is called the Battery 500 project. The challenge of achieving this is mostly related to the carbon. I mentioned earlier the carbon takes up half the volume of the cell. Ideally, we'd like to make lithium work, but if that doesn't work, we have a number of other opportunities. So, we have shown that tin-iron alloys look very well. We have to use more lithium in the existing materials, so we can get more lithium into the material. It will store more energy and will cost less as we'll be using more of the transition metal here. The other thing we'd like to do is make the electrodes much thicker in order to do that, we have to have materials that are much better ionic and electronic conductivity. So, in all these materials on this slide, we have to mix these cathode materials with carbon to make them conductive, unlike titanium disulfide, which is itself a metallic conductor. So ideally, we'd like a very highly conducting cathode material so that we'll be able to get this energy density quite a lot higher.

So, let's just look at what the challenges are now. I’ll start off with the layered oxide materials so you can see where we're going, where we've come from. So, let me go back to this. Let’s start with a figure here. All these materials are layered structures. You can call them sandwich structures if you like, where the metal oxide is in the blue and the lithium ions are yellow. So, all we're doing is moving lithium ions between these sandwiches in here. So, we take them all out and essentially no bonding, and then we can insert them back in. And the lattice just expands and contracts by about 5 to 10 percent. So, this is a chemical formula, and I've just shown you there are two oxygens up to one lithium and then a range of different metals, and we typically call these NMCA, nickel, manganese, cobalt, aluminum. And for electronics, it’s essentially still pure cobalt. This mixed metal material now dominates most electric vehicles, energy storage, but there's a huge push on research-wise to eliminate the cobalt, preferably all of that, all of it, but certainly up to 90 percent of it. This is due to cost and environmental issues, as well as the child labor issues I mentioned earlier. The nomenclature we use for these materials is shown here. We describe them maybe as 333 or 622, and I show you what I mean by that. 622 means it's 0.6 nickel 0.2 manganese, 0.2 cobalt. And the trend in electric vehicles has gone from 333 to 622, and a number of companies are now using 811 and certainly LG and others are using 811 in their cylindrical cells. And it's been recently reported that Tesla is now using 90 percent nickel in their NCA.

The real challenge we have is one that worries a lot of people. If we want higher energy, we have then decreased safety. And we can see that by looking at this, I’ll call now, famous plot. This comes from Dr. Sun's group in South Korea. What we want is high thermal stability, so we want to be up in this top area here, but we want high capacity, which means we're over here. Where we want to be is up in this top circle. So, we got high thermal stability, high capacity, and the capacity is retained for a long time. What is the challenge if you want high thermal stability? You've got only one third nickel. If you want high capacity, you got 85, 90 percent nickel. So, the more nickel you put in, the higher energy goes, the less thermally stable the materials. So, there is a lot of us working to get into this third blue box. And I'll show you some of the data we've got on that in a moment.

One of the ways to help solve the reactivity, which is related to safety, is to put a few percent aluminum in there. That stops all of the lithium from being removed, but it reduces the capacity. For future effort, it would be ideal to use much more manganese, as it is by far the lowest cost. So, I imagine everyone's trying to get the cobalt out. As we get the cobalt out, the next most costly element is nickel, so people would like to remove that as well.

So, let's look at where we stand on this material. So, our goal is to get into this blue circle. And this is work from the Battery 500 consortium, and this is based at the Pacific Northwest National Lab in Washington State, and we started out as our baseline materials is 60 percent nickel and our consortium all use the same material. And the material came from Ecopro in South Korea. So, it's one of your materials. And our initial goal was to achieve more than 350Wh/kg. And obviously we've achieved that. But the type of material working with what we call these meatball materials, so you can see these meatballs here. They're are about 5 to 10 microns across. And they’re comprised of these much smaller primary particles, which are maybe 100 or 200 nanometers.

So, let's look at the progress we've made over the last four years. So, you can see in 2017, we got about, I guess, 50 cycles out of this and we got 300Wh/kg. By 2018, we got to over 200 cycles. And in 2019, we now push this up to 350Wh/kg and also about 250 cycles. And as of last September, we've now got 350Wh/kg and we're somewhere over 400 cycles at this point. This material has a volumetric energy density of about 700Wh/L. And there's no adjustment to this data. This is actual data. This is cells built by an ex-student of mine Jie Xiao. He is at the Pacific Northwest National Lab and the cells were tested at the Idaho National Lab. And you can see this data in the Annual Merit Review (AMR) of DOE, from Last May. So, this is the typical pouch cells we're using. These are 2Ah, we're going larger now. And to get the energy densities, we weigh this cell and we measure its size. So, there's no fudging the data, no extrapolating it to higher sizes. So, these are real data that we got out. But this is still not good enough to get us to 400 and then to 450 and 500.

So, what we have to do with these structures is use all the material. What do I mean by that is all these layered oxides, if you charged them up, you get about 230mAh/g on the charge. When you discharge you’re losing over 30mAh/g, so you're losing somewhere between 10 and 20 percent material on the very first cycle. We can't afford to do that because this is capacity at the most stable part of the electrolyte. So, we need to recover that. So, we've been looking at what causes that problem. What we found was the lithium ions diffuse very slowly as we fill the lattice up so you can think of this as a lecture hall, two thirds or three quarters full of people. So, you fill it up quite easily to begin with when you get about three quarters full. Then you see a diffusion coefficient falls off rapidly. In the lecture hall then, people have to start moving at this stage, so you fill up all the vacant seats in the middle. So, this is the real challenge is “Can we solve this problem here?” You can take out all lithium very easily, just as you can empty a lecture hall very easily. So, there's no problem in fast charging these materials.

So, we looked at can resolve this? and What is some of the real issues? So just to summarize, a few of them, what we looked at is changing the temperature, to increase the temperature where the ions move faster. And on the left-hand side, these two plots are just the same curves I showed you before. We charge to four different voltages, so we charge up to 4.2, 4.4, 4.6, 4.8. And we discharge it. And you can see this is the loss we have. But if we hold the battery at this lower voltage for several hours, we get a lot of it back. So that's just flat plateau. So that, again, tells us diffusion controlled and if we increase the temperature from room temperature about 21 to 45, you can now see this red one compares to this red one. And you can see this loss here is much less, the same as 4.6, but if we go to 4.8 volts with the higher temperature, the battery is now unstable. We're getting a lot of side reactions and loss of capacity. So, we know that raises an issue, but we also believe it's something to do with the structure and not necessarily the whole structure. So, if you look at lithium-cobalt oxide, it does not show this first cycle loss.

If I look at this 80 percent nickel, the black is room temperature, the red is 45 and you can say it's much better behavior at 45 and this shows there is a blow up in this area down here. So, in this case, we held it for one hundred hours. And you can see we can fill the whole lattice up with no problem. So, it's just very slow diffusion. If we now look at lithium cobalt oxide, the blue is room temperature, the purple is 45, there's no difference here. So, lithium cobalt oxide has almost the same structure, so we thought they should behave the same. So, our goal was to modify this layered structure, to make it behave more like lithium cobalt oxide. And we do this by substituting and doping it with another element. And what we chose to use was niobium. I don’t all the detail here, but we put either 1 percent, 2 percent or 3 percent niobium solution on the material, heated it up, and the brown here shows where the niobium is and that diffuses into the surface a little bit. And, you know, just from these curves here, the black curve is no niobium, we brought 1 percent to 3 percent in, we were halving this first cycle loss. So clearly, we can modify the structure to reduce this loss. I'm still working on this and hope to totally reduce it.

Let me move on from this compound. And talk about a little bit more of the history, so you can see where we've come from. So, we started out with titanium sulfide. Moli Energy and Jeff Dahn were in British Columbia, Canada. They switched out titanium disulfide and put in moly disulfide because Li-moly disulfide is molybdenite, a naturally occurring mineral in British Columbia. So, they're able to get that and that company commercialized this material. And it was for sale for quite a few years, but they had a few accidents with dendrites and they eventually went off the market and has changed hands a number of times and is now a standard lithium ion company. And then switch to cobalt oxide—I've already mentioned that—and to the mixed oxide, and then John Goodenough came up with lithium ion phosphate, and I show you the structure of lithium ion phosphate here. Again, I won't go into any details except to say this is what we call a tunnel structure. It is a very stable structure and it is much safer than the layered oxides. Layered oxides can give off oxygen and cause fires. This material does not give off oxygen and the lithium ions reside in these tunnels. And this has no first cycle loss. So, from the second cycle to the 1,000th cycle, this material behaves almost identically. So in a sense, it's an ideal material, but it has much too low energy density to be useful for portable applications, or for most of them.

My colleagues are now looking again at 4V lithium manganese phosphates. Lithium-ion phosphates you can see here is about 3.4 volts. Go to manganese. We can then increase the energy density somewhat. And this is the materials that Michael Graetzel worked on in Switzerland and then it moved to the US. I said the energy density is way too low for these materials. So, we've been looking at, Can you now place two lithium ions into this structure so we can increase the energy density without increasing the volume of the material or its weight? And obviously, I wouldn't be talking about this vanadium phosphate unless it had succeeded. And this was one of the accomplishments of the large EFRC (Energy Frontier Research Center) and that would say most of the big successes in science today are collaborations between the US—that's the federal government—academia here, and national labs. So, we had in here a number of universities, a number of national labs all working together, a mixture of disciplines, experimentalists, theorists, like good large-scale characterization people.

And this was successful, it was highlighted in the White House's report of the accomplishments of the year 2018, and here are two of the students, one of Clare Grey's students and one of my students, receiving a plaque from the Undersecretary of Energy in July of 2019. So, let's look at what this material is. Again, it's a tunnel structure. It has the advantage of iron phosphate in the sense that lithium ions can go in all three directions, so the tunnels don't get blocked. So, I show you the structure here. Phosphate tetrahedral, vanadium oxide distorted octahedra with a network like this, and we know we can stick two lithiums in here. The question was, “Can we put them in there and take them out hundreds of times without destroying the lattice?” So, it took us quite a few years to make material that was electrochemically active, and we make these materials now we know how to do it. Basically, a solution. So, we dissolve vanadium compound, phosphorus compound in ethanol, to which there is a small amount of water added. Water stops of vanadium being over-reduced. And we just heat this up for one to three days. Then we get this structure here, with a lot of protons in it. So, we have two protons here. It says two lithiums here, I showed you they were there. We gently heat this. All the protons come out and we now have an empty lattice.

One of the things we tend to do in the battery area, we want to understand the structures, it is much easier to do structural studies if you have a clean, pure material. So, when we're at Exxon, we developed a number of what we call chemical techniques of putting lithium into materials and for taking lithium out. So, we use this organic reagent, beautiful lithium, clear straw colored, so you can see what's going on and you can actually follow the reaction in an optical microscope. So, we're able to react this material with… …was feasible. I think what was critical, we showed that when we put two lithiums in this lattice that only expands by just over 8 percent. So, not much different than the expansion of graphite or the expansion of the titanium disulfide. So, we were able to show that this should be feasible. We're able to characterize these structures and understand them. And for those new to the field, when we developed this technique, you could also easily measure the temperature of reaction, so you just put a regular thermometer or thermocouple in the beaker, which is obviously a glove box, and how quickly that beaker heated up told you the power capability of these materials.

So, let's look at what we made. So, this is the type of material we make, little cuboids all roughly the same size. With then coat, these was graphene to make it conductive because these phosphates are electronic insulators. And I show you the electrochemistry on the right-hand side here. Again, I won't go into any great detail here. Because we're trying to lithiums in, we have two different voltages. So, we have one voltage about 4V up here, and the second one down here, about 2.5V. The key thing to note here is the black line is the first time we do it, the purple line is the 50th time. So, anything the material behaves better the 50th time than it does the first time. So, we have proof of concept that you can, in fact, reversibly intercalate two lithium ions into a crystal lattice without damaging that lattice. That's not to say everything is simple and solved. We still have a number of challenges with this material. I'll just touch briefly on one of them here to make a point about most battery materials. As I showed you, this is, we have, one reaction up here, another reaction down there. If we look at this high voltage reaction, this is what we call a two-phase reaction going from $VOPO_4$ and putting one lithium in. We get a flat voltage plateau here. But as we increase the rate of reaction, we lose energy density. So, this is slow diffusion, just like it was in those layered oxides. And this just shows you the same data. Here is our capacity drops off fast as we increase the rate. So, for those not familiar with the field, the C-rate means it's one hour. C over 50 means it takes 50 hours. So, when we slow the reactors, we get much higher capacity than we do if we do it fast.

In direct contrast, though, we go to this low voltage regime and this is in this regime down here. Down here, we can now see these curves almost on top of each other and the capacity is the same, no matter how fast or slow we do it, from 50 hours to one hour. The capacity is the same. And you can see this plot is on the right-hand side over here. So extremely high rate for the lower voltage, but low rate for the higher voltage. And this is related to the fact that we have what we call a single-phase reaction where we put more than one lithium in, so lithiums are not ordered in any manner. So, what we're trying now to do is modify this structure, just as we did with lithium ion phosphate, to make it behave like a single-phase reaction at the high voltage as well.

So, let me conclude with two or three slides. A few of the battery folks in the audience may have noticed a gap here. We have some oxidative issues with the electrolytes. We are changing the electrolytes as well.

So, where do we stand in in the battle here? What's going to happen? These lithium intercalation systems are going to dominate the next 5 to 10 years. I don't think there's much question about that. The layered oxides will be the dominant one amongst these. Phosphates, where there is iron, manganese, or vanadium. We think the market is going to increase for those. It costs less in euros, dollars, whatever currency you use than anything else. And the real issue that I think is limiting a lot of the layered oxides is the stability of the systems. We need safer and more stable electrolytes. The electrolyte really hasn't changed since 1990, and the question is, “Can solid-state give us the required power densities?” because in principle, solid state should be much more stable. But there are a number of issues clearly coming up as we worry about climate change. We need new manufacturing technologies. So, today to make a new 1KWh battery, it takes between 60 to 80KWh of energy. We need clean recycling technologies, so we can recover all the cobalt, lithium and the other elements to give us a sustainable society. And I think equally important, we need regional supply chains and manufacturing. It doesn't make all that much sense to ship the materials around the world two or three times before the battery is made. So, for example, you may mine graphite in Australia or Africa, send it to China to be cleaned up and send it back to South Korea or America or Europe to make the batteries. We need a regional supply chain. And Europe is a great example. They’ve in the last three or four years put a large multibillion-dollar program in place to integrate everything from the mine to the product and with the intention of doing the most energy intensive work in Scandinavia, where they've got lots of clean hydropower.

Let me just raise a couple of questions. I call these unknowns. They are things really without an obvious solution. What puzzles me is why are the lower cost and safer phosphates not used more for electrochemical energy storage. And I think all the South Korean companies, as well as most of the US ones, are using the oxides for storage. Phosphates would be better. Initially in the US, A123 used lithium iron phosphate, but the same companies are now all using layered oxides. There's been a slight change in the trend since Tesla announced they are going to use lithium iron phosphate for their cars. They manufacture in China and they're shipping those cars off to Germany for sale. And they've announced that the lowest cost cars in the future in the US will also use lithium iron phosphate. So, the question I really raise is, is energy density is so important that people will not be willing to use the phosphates? And if that's the case, then this will essentially eliminate all not-lithium technologies because lithium clearly has the highest energy density.

I already mentioned we need safer and more stable electrolytes. There are some solid-state batteries in production, being used now. And this is the Mercedes bus I mentioned earlier. The question is, Can the same polymer-based cells be used for non-fleet EVs? All the present solid-state cells are used either by the Bollore Cars, which are fleet cars you rent by the hour, or in things like buses and some trucks. Blue Solutions who make the batteries here believes so, and they say they will be making batteries that operate around room temperature by 2025. And they'll be going in vehicles by then.

Let me just finish by three points that I made on behalf of the Chemistry Laureates just over a year ago, and this is, I think, particularly important for the younger members of the audience to remember: the science is interdisciplinary. Science does not neatly fit into chemistry, physics, mechanical engineering or whatever. It crosses all those boundaries. And science is also international. Again, it knows no boundaries, so Gerbrand and I are in the US, you're all in South Korea. And I make this point because if you look at the Nobel Laureates, I'm a chemist, John Goodenough is a physicist, and Akira is an engineer. Look at the geographies. I was born in the U.K. but made my inventions in the United States. John was in fact born in Germany, but is an American, and he made his major inventions at Oxford in England. And Akira made his inventions in Japan. So, three different continents were involved. And that's quite often what is needed. Let me emphasize again, energy storage is enabling renewable energy. It’s going to mitigate global warming and messing up, and it’s going to let us have a more efficient grid.

And two other points I really want to make is, we have to understand cultures because Americans, Europeans and South Koreans, we don't all think the same way, we don't all act the same way. We have to understand how each one of us responds to requests. And I know. Most engineers in the US will stand up to their bosses if they tell them to do something they feel is not safe. I think maybe some companies in South Korea learned the hard way when number of batteries caught fire. The engineers have to say, “Stop. We can't push more energy into a given box.” And the other thing, clearly, that's been an issue in the last three or four years. Facts matter and science matters. And I'll stop there. Thank you all very much. And I'll come back in a while to answer questions.

현택환:

Thank you very much for your wonderful presentation, Professor Whittingham. Professor Whittingham will join us later for the discussion session. Let's move on to the second presentation.

The speaker is Professor Gerbrand Ceder. He is Daniel M.Tellep Distinguished Professor of Engineering at UC Berkeley, where he developed novel materials for energy storage. He has worked on the lithium ion battery for more than 20 years, and recently he's also working on alternative energy storage approaches such as all-solid-state batteries. He's a member of the National Academy of Engineering of the United States, and also he is a member of the Royal Flemish Academy of Evolution for Science and the Art. And he also he is also the lead scientist for new battery technology at the Joint Center for Energy Storage of the United States Department of Energy. And I think it's one of his biggest contribution to science and engineering in general is that he convinced the Obama administration and White House and he initiated so-called materials genome initiative, which is actually instead of conducting a thousand experiments, actually, he used computational science to design new materials, such as new battery materials and solar cells and thermoelectric materials. That is one of his biggest contributions to science and engineering in general. Today, he will talk about “Disordered Rocksalt: Resource Friendly Cathode Materials.” Professor Ceder, please.

Gerbrand Ceder:

Thank you so much. Well, thank you so much for the invitation. Let me get this in full screen. There you go. And I really wish I could be there. I love coming to Korea. It is a country that has been so friendly to me and so enjoyable, all the interactions I have there. So hopefully soon, in better times, we will meet in person again. So, Professor Whittingham gave a wonderful introduction on the many of the important aspects of lithium ion and telling you where they came from and how they operate. So, what I'm going to do today is look a little forward and look at some of the challenges we have and how we can solve them. As was already explained, lithium ion today is everywhere. It is a remarkably successful technology. I think that 30 years ago, I doubt that anybody would have expected it to become so big. It went from phones to power tools. Today, I'm quite the hobbyist. Every power tool I have are cordless these days is with the lithium ion because they are so much better things you have to plug in. But then, of course in vehicles and even in the grid.

And you've seen in Professor Whittingham's talk an introduction to typical cathode materials for lithium ion. And I'm sort of reiterating them again here. Right? Layered structures, lithium ion phosphate, and then, of course, also the lithium manganese oxide spinel. And all these have been commercialized in some form or another. What all these cathodes have in common is that they are well-ordered structures. So, the metals are in well-ordered positions and that creates well-defined pathways for lithium to go in and out of these materials. So, in a layered material, lithium diffuses in and out of the layer. And that's how you charge and discharge in lithium ion phosphate. It goes in and out of these tunnels and then lithium manganese oxide spinel, it goes sort of in and out of tunnels but the tunnels are three dimensionally connected, just like the ε-VOPO4 material that Professor Whittingham showed.

And I have been for quite a while trying to come up with new battery cathodes. And, you know, for 20, 30 years, we have looked for other materials in this category of well-ordered structure and we have found many materials that work. But it's extremely hard to find things that are better than these materials that exist today. And I want to show you an example that ordering can be somewhat limiting in the chemistry we use. Again, Professor Whittingham introduced you over to the NMC series, which really started with lithium cobalt oxide. And then as you replace cobalt by nickel, you get to the higher nickel contents and NMC811 is 80% nickel. And these days you can even go to 90% nickel. But you can ask the question, why have we not made layered materials with many more different metals? There are many other transition metals that would be much less expensive than nickel and cobalt, so why don't we make layered cathodes from these? And the reason we now understand is the following. Here is a cartoon of a layered structure. So, what you do in a lithium ion battery when you charge is that you sort of pull the lithium ions up. Most of them. You don't pull all of them up. Most of them. And then you have all this free space here. And what happens with many metals is that they migrate and they go and sit in the space of the lithium that contracts the structure and now becomes very hard to put lithium back in. So, it turns out that the only metals that really don't like to do this migration is cobalt and nickel and to some extent manganese. And to come back to the point that Professor Whittingham made, that this is a very interdisciplinary field, this is the reason that nickel and cobalt are so good is really not an engineering issue. It is a purely physics issue. It is because of their particular electronics structure. Cobalt, Nickel IV, Nickel III, and Manganese IV have electronics structures that really favors that octahedral coordination, which is what they have when they sit here. They are coordinated by six oxygens. And so, because they're so happy there, they really do not want to migrate. And that's why these layered materials are so stable against migration. If you do that with other elements like Manganese 3+ or Iron or Titanium, what you will find is after you do a number of rotation cycles, you will see that the metals migrate. So, it's a very sort of physics determined, very intrinsic property of these layered cathodes that you can only make operating them really good with nickel and cobalt.

So, the question is, can we sort of use layered materials and keep on doing this and can we keep on scaling the lithium ion industry with layered NMC cathodes? And this depends a bit on your perspective. Personally, I think that lithium ion is a real winner in energy storage. It has become extremely good. It's also become relatively safe and relatively inexpensive. It used to be a thousand dollars a kWh and today it's really one hundred dollars a kWh. So, I think that we will see it going big time in many applications. So, here's a prediction from benchmark minerals that claims we will go to 2TWh of production by 2030. As any research in Korea comes to it, about 3.4TWh. And then, of course, our friend Elon Musk, always wanting to think bigger, thinks we will actually be making 20TWh of energy storage by 2030, 10 for grid and 10 for automotive. I just want to put that in perspective. You may think that's a big number, but 1TWh is actually not really that big. It's about 12 million EVs, if you count any of at about an 85kWh battery, which is kind of a large Tesla. And so that's barely a little over 10% of annual automotive production each year. It's also just China's electricity production for one hour. So, with all the batteries you make with one terawatt hour production a year, you could back up China's electricity production for simply one hour. And of course, it's a hundred billion iPhones and we won't be needing that many of them.

So, the question is, how much do you need in metal? Well, order of magnitude, if you want to make kilowatt hour, you roughly need 0.8~1 kilogram of combined cobalt nickel. And depending on whether you make lithium cobalt dioxide or high nickel NMCs, you would need more cobalt or more nickel. So that means if you want to do a terawatt hour, you need a million ton of some combination of these metals. And of course, if you want to be Elon Musk and do 10TWh with NMC, you'd need 10 million tons of nickel and cobalt of annual production. So how do we how are we doing? Well, obviously, we're not going to do this with cobalt. Here's the cobalt annual production extrapolated into 2013. And the number for 2020 is around two hundred kilotons per year. So basically, if you were to just use cobalt, you would barely be able to make 200GWh. So, a few percent of car production could be it, that's it. Now is nickel much better? Of course, the world production of nickel is much higher. Actually, in 2020, world production of nickel was about 2.3 million tons. So, you could say, well, we will take all of that nickel and we'll make lithium ion batteries with it. And so, we're good for 2TWh. Well, I don't think the rest of the world would let you do that because most of nickel today goes for stainless steel. It is a critical ingredient in stainless steel and cannot be replaced. And that uses at about 1.6 million tons per year. So, if we want to do, say, 3TWh based on nickel, we will need about 4~5 million tons of nickel production by 2030, which is about double of what we will do today. So, it's hard to imagine that nickel and cobalt alone can be a long-term strategy for the lithium ion industry. And it's not saying that these NMC materials aren't good. They are really, truly fabulous materials. But resource wise, they really could become an issue.

So, in my lab, we have been for a long time combining computations and experiments to try to come up with materials and the computational side was really revolutionized in the 1960s by practical solutions to quantum mechanics and ideas, of course, that we understand the basic laws of physics. Right? We can write them down in some form, but that doesn't mean you can solve them. But using powerful computers today, we can solve the laws of quantum mechanics approximately, but accurately enough, and then we can make predictions of how materials behave. So, imagine this a bit like an in-Silico laboratory. And about 15 years ago, we realized, well, you know, if you can compute things once, you can compute the many times. And that led to what we call now high throughput computing. That is, that once you develop algorithms to make computations on, say, voltage of the material, you can kind of cue up 10,000 materials and come back the next morning or maybe the next week, depending on how much computing time you have, and get results for it. Because computing, of course, can be quite easily automated. And this path of discovery led us to what we now call disordered rocksalts. And I'll go quite a bit more in detail on them, into why they will bring chemical diversity and also quite high energy density. But one issue with them is that because they pack the oxygen so closely, like in layered materials, that can have in principal very high energy density. So, unlike a layered material or lithium ion phosphate, these materials sort of look a lot more complex. The oxygens are nicely well arranged. They still form a crystalline material. But the cations which are in this case, I show three: the manganese, some titanium, and the green is lithium. Those are all disordered in the structure. So, they sit in octahedral cavities, but they don't take any particular pattern. And so, the question that we had is, first of all, if you could make this work, this would be fabulous. Right? Because the reason we need specific elements like nickel and cobalt is because we want them to take on a particular order. If we don't have to care about the ordering anymore, then we can actually use many more transition metals. And that could solve, in part, the problem of resource scarcity. Right? If maybe we can use manganese, maybe we can use iron, or/and maybe we can use more titanium.

And so, the question is really, if you don't have these well-defined pathways as layered materials, can you still have diffusion of lithium in and out of a structure? And maybe to reiterate the point that Professor Whittingham made earlier, you know, batteries is truly an interdisciplinary field. It's not just about electrochemistry or about synthesis or about physics. It really combines a lot of these things. And you never know where an answer will come from. So, it turns out, even though we invented these materials only 5, 6 years ago, the the groundwork for them was laid by two really very bright graduate students I had. And one of them you actually know, because he's actually going to speak at the symposium later, Professor Kisuk Kang, who's, of course, at Seoul National now, and Professor Anton Van der Ven, who's at UC Santa Barbara now, really had both worked on how exactly this lithium diffuse through all these structures. Looking at the detailed microscopic mechanism of how it diffuses. And what we learned is that it hopped from one octahedral site where it likes to reside, to another site through the connecting tetrahedral. You see this here, in this figure, it always has to hop through there. And what really matters for setting its mobility is the other ions that are close to that tetrahedron. And so, what we learned from that is that if you disorder material, you get all these different environments around the tetrahedron. Again, inside here is the critical point. That's how lithium has to sneak through from one to the other one. And while in many cases you have transition metal sitting around and lithium doesn't really like them because a transition metal is high charge (is 2+ or 3+ or sometimes 4+). And when lithium wants to diffuse through the tetrahedron in really because of electrostatic interaction, it really doesn't want to be close to that. But if you disorder materials, then you statistically find other environments as well, and one we were particularly interested in was actually what we call the zero-transition metal environment or 0-TM environment. Let's say this site is vacant. When lithium diffuses through here, it really only sees other lithium. So, it sees just very low charge coming from these other lithium's. So, it would not see a lot of repulsion. Now, of course, you may be able to hop through there. But the real question was, can you then statistically percolate that through a structure? And that's what Jinhyuk Lee, also a Seoul National student and now at McGill University, figured out is that if you had enough lithium in the material, you would create enough of these environments and they would statistically start percolating through the structure (what is shown here). And lithium could essentially through a slightly twisted path get still in and out of the structure rather than through these well-defined paths that you saw in the layered materials. And we find typically that we need at least 10% excess lithium, sometimes even 20% excess lithium to make this work. And this does work. Here, sort of a proof of concept. Actually, if you see the background behind me, that is a transmission electron microscopy picture of a disordered rocksalt. And the reason it looks so boring is because the structure is very boring. It's really just intensities everywhere and that's because lithium and the transition metal are mixed. In diffraction, you see just a normal rocksalt. And remarkable. Even though this is not an ordered structure, you can cycle the lithium in and out of this material (as shown) up to about 20 cycles, charging all the way up to 4.8 Volt. And this is a nice energy content for the cathode. It's not spectacular. It's not as good as NMC. But it's sort of better than lithium ion phosphate. But I'll show you some better materials later on.

But the promise of...Remember why we do this, right? We want to make disordered materials so we are not constrained by particular transition metals. And that has borne out. I collected, a few years ago, many of the what we now call DRX materials for disordered rocksalt, lithium-excess materials. And basically, almost every possible redox couple has been activated in these materials. Of course, the nickel ones, the cobalt ones like you can do in layer materials, but also the two manganese redox couples, the vanadium redox couple, even the iron redox couple, molybdenum, chromium and even, of course, the oxygen redox couple. So, basically, we now have a whole structure in which we can use almost the complete periodic table. We can get good specific energy. So, energy per unit weight, which is what these numbers are, we can go up to almost 1000 watt-hour per kilogram, but that's only in the initial charge, discharge cycles. And I'll show you some of the challenges that still remain with these materials.

So, where are we now? So, by making the sort of rock salts, we can use many different elements so we don't rely on a single metal element. I'll show you that can also lead to cost reduction. But I think what's really important is that because we can put many, many elements in the structure, we actually have a very large design space in which we can optimize. We can make almost all things soluble in these materials. And this is important because I think today, we have only scratched the tip of the iceberg because we have only optimized a very small part of the subspace.

So, I'm going to show you a few examples of how we use this chemical flexibility to actually optimize the structure. And the first one is actually not cations substitution, it's actually anion substitution. This was somewhat to our surprise, we could actually substitute a fairly large amount of oxygen by fluorine by solid-state synthesis. We could do about 10, 15%. If we do extensive modeling, then we can go all the way up to 35%. But fluorine turns out to do very interesting things in these materials. So, here's the anion group. Every time you replace an oxygen by a fluorine, you lowered a negative charge in the unit. And that means you also to charge compensate, lower the positive charge. So, by putting in a lot of fluorine, you can lower the charge on the transition metals. And that, of course, means you have more room to oxidize because oxidizing means you raise the charge of the transition metal. Or if you're doing it at fixed capacity, it means you don't have to go so high in oxidation, which makes the material safer because it's the high state of oxidation that makes the material somewhat more unsafe. So, if we go to very high fluorine content, here's a material with 30% fluorine substitution to the oxygen, we can go all the way down to Mn 2 in a rocksalt, which is a bit unusual. And so that means we can oxidize 2 to 4. We have a new double redox couple. And in the past, we don't have that many double redox couples. In NMC materials, you have nickel 2 to 4. Professor Whittingham showed you the vanadium redox couple. There are not a lot of double redox couples. But in some sense, a double redox couple is double bang for the buck. Right? You can get two electrons for the price of one metal. And you see, we can get very high discharge specific energies approaching 100 watt-hour per kilogram.

Fluorine substitution also significantly improves cycle ability. Here's a manganese niobium series, and here we have a pure oxide. We lose a little bit of capacity every cycle. We get about 700 watt-hour per kilogram. We go to even just 0.5, so 2.5% fluorine, that specific energy goes up quite a bit. Cycle life improves, but is not good enough yet. But by the time we reach 5% fluorine, so 0.1, we actually get much better cycle life in the material that's also been shown by others. Here's a paper by Wei Tong on high fluorine manganese niobates. And this is essentially cycling between the same voltage limit, but as you put more fluorine in, you actually see the capacity retention becomes much, much better.

We kind of know why that is and we see that in other sets of data. One issue with materials when you charge them to high voltage is that they tend to be over oxidized and and they release oxygen gas. Professor Whittingham talked about this already, which is a major safety issue. It is also a degradation issue. And if you look at a commercial NMC622, so this is a commercial well-optimized NMC., you lose a certain amount, (you don't have to worry about the units here, it's actually millimoles of gas per mole of material), about 0.4. If you take a commercial lithium rich NMC, you get about 1. As soon as we dope even 2.5% fluorine, and these are not optimized materials, they are actually a much higher surface area material. So, you would expect them to lose more oxygen. We're already close to an NMC-622. But look at this. When we go to 30 percent flourine substitution, we have undetectable oxygen release. We do not see any oxygen coming off, even though we charge to 4.8 Volt. We've actually even gone to 5 Volt and there is no oxygen whatsoever coming off. So, fluorine seems to clearly protect the surface of these materials and prevents any sort of outgassing coming from the material. We see that in STEM data, this is actually work from Chongmin Wang and his post-doc Linze Chen of China Pacific Northwest National Lab. We've done some beautiful work on these materials. This is pristine disordered rock salt, just an oxide. After you cycle it 50 times up to 4.8 volt, you actually start to really see holes in the material. So, it's a bit hard to see on this picture. These are actually voids. And if you look at the EELS from lithium, you actually see that there's truly material gone. So, these things have truly pit corrosion. When you fluorinate, so this is about 2.2, exactly the same charge protocol, you get a perfectly retained rocksalt up to the surface, no surface degradation whatsoever present. So, the materials seem intrinsically stable once they're fluid and at very high potential. But that doesn't mean that all problems are solved, as I will show you later.

One more example I want to give you about DRX materials is how you can use the compositional degrees of freedom to improve them is that when the first DRX materials were published by ourselves, by Yabuuchi in Japan, they actually had very little rate capability. People had to heat them to almost 60 degrees to get reasonably high rate capability. So today, we actually have several strategies to obtain a very high rate capability and we can even go up to one ampere per gram, and we do that by using concepts from modern alloy theory to engineer high rate capability. So, the way we do that is to actually think about what happens in these real materials. So, remember that I told you that we really want these channels, what are called 0-TM channels. What actually happens when we think we make a disordered rock salt is that there's something called short range order. And what short range order is that there's some statistical correlation that deviates from randomness. So, when you think you might get a lithium nearest neighbors, the system actually prefers to make lithium-safe transition metal neighbors because these have sort of opposite relative valence. And what you see that whenever a transition metal goes and sits here, you lose this beautiful channel to diffuse through because as soon as there's any transition metal here, you can actually not diffuse lithium through. And so, what we found is that this short-range correlation, the fact that it's not perfectly random, actually destroys the lithium diffusion in these materials. And to show you really nice examples of two materials that are almost the same compositionally, there's a 20% lithium excess rocksalt with 0.4 Manganese. And either we dope in zirconium as a stabilizer, so there is a 4+ element or we replace it by titanium, so just another 4+. Right? So, electrochemically, these materials almost look the same. But if you look at them in TM-electron diffraction, the dark spots (that's the basic rocksalt lattice, so don't worry about this, it's the same in every structure) but you see this sort of diffuse fuzziness that's actually caused by cation short range order. And what you see that it's very different with zirconium than with titanium. Here, it's almost circles. And here you get these kinds of squares. And we now know that that's because of very different short-range correlations and at least two very different performance between the materials. This material performs very badly. The titanium one performed very well, even though they're the same particle size, they're almost the same material. And if you do simulations, you actually see why that is. If you calculate, simulate this material at its synthesis temperature and you plot the 0-TM percolation pathways, you see that's in zirconium, it's these green things is actually quite bad, it is very sparse. In the titanium, your short-range order is much better. And it contains a lot more of these channels. And you have very good percolation and therefore very good diffusion. OK, so now that we understand this basic science, how do we fix this problem? Well, we try to use a theory that's been out there in metallic alloys. You know, if you follow the literature of metals, it's sort of been revived by this concept, what we call high entropy metal alloys. So what high entropy metal alloys are is that basically people have shown that if you add a lot of different metals to a base metal, you can actually get much higher solubility. So, what I mean with that is, for example, if you say 20% of a substitution, 20% of doping in a metal, it's very different. If you do 20% of just one metal or or 1% of 20 different metals, 1% of 20 different metals is what's called a high entropy system and creates much more randomness, which can be used to improve performance. So, we thought, let's try that with these DRX materials. Let's see if we can do high entropy to kill the short-range order and improve rate performance.

So, I'm going to show you three materials where I systematically increase the number of metals I put in the system. So, this is a 1.3 or 30% lithium excess system, the fluorine content is always the same at 15%. And TM-2 is the material with just manganese and titanium. So, manganese is redox active, titanium is a stabilizer. And you see very pronounced short-range order in the direction (the sort of fuzzy things). The capacity is good, it's respectable. It's about 700 watt-hour per kilogram energy. But let's see what happens if I now start increasing the entropy. So, if I split the manganese into 2+ and 3+, which will give me some electronic entropy and I split the titanium between titanium and niobium, we make the material exactly the same conditions. You're seeing we're already starting to reduce the short-range order. And remarkably, the performance goes up at the same current, we're already getting more discharge capacity and higher energy density (already at 850 watt-hour per kilogram, which is very good). So, the question is, can we keep on going? So now we're throwing the whole kitchen sink. We use manganese and cobalt. We use chromium and manganese in the other state. And then again, titanium. Now, we have six transition metals all mixed together and now we have no short-range order anymore. So, we now truly have a random system. And now our discharge capacity is 955Wh/g, which is very high for a rocksalt. NMCs are kind of in the 750 range. So, it's interesting how an idea that is sort of transferred from another field by understanding the basic science, how you can introduce that into the battery field. What's remarkable is that this is a very high rate capability, unlike some other DRXs. So, we can discharge this up to 500 million parts per gram. We still get good capacity and we've even done 2 amperes per gram and still get good capacity of this material. These particles are all sort of similar size, about 150~200 nanometers.

OK, so the last example I want to show you is what I call "Living on the Edge", which is working with partial disorder. So, for a long time, we all have worked with ordered systems and I explained that before. And then about five or six years ago, we said, oh, let's randomize the cation. If you think of this is a large configuration space, we worked with totally random cations. Well, in reality, they weren't truly random. They were somewhat short-range order. So, they kind of live around this space of random. So, the question is, can we also make interesting cathodes by making partially disordered structures? So, these are materials that are still long-range order, but you introduce a lot of disorder in them to try to optimize some properties. And the material we picked is a spinel. And the reason we like spinel is because spinel, even in the ordered state, already has some of these 0-TM channels, which is in part what's responsible for the very good lithium mobility in spinel. So of course, spinel has been commercialized. It didn't do so well. And the reason is, of course, that if you look at the full discharge of a spinel, this is Nm2O4, this is Li2Nm2O4, so spinel sits here. Commercially, one can only use this part. And this is exactly for the reason that Professor Whittingham mentioned in the VOPO4, as well, this material is this region is largely a solid solution. We know intercalation salt solutions work quite well. This cycles quite well. You would really like to use this extra capacity. Well, it turns out this is also a two-phase reaction, just like what he showed in his VOPO4. And we don't like 2-phase reactions because they often have slower kinetics. The other thing is that this 2-phase reaction is a large volume expansion, which is also not good because it degrades the cathode. So, what we try to figure out, can we go to partial disorder and kill this 2-phase, can we essentially make this an all-solid solution? And of course, the physics community has figured this out. They have whole theories about how much disorder you should introduce to kill first-order transitions, which is what a 2-phase reaction is. And again, you do that by starting to introduce disorder. So rather than make a perfect spinel, we want to make one where the manganese is slightly disordered but also that's over stoichiometric in cations, especially lithium. And so, what we really want to do, which is a bit difficult, is we want to make a material in this 2-phase region where we have excess cations because we know that gives the material very good mobility from work on lithium titanite and spinels. So, basically what we do is we disorder the material, we also induce excess lithium and for good sports, we also introduce some fluorine into the material. So, I'm going to show you two materials which are quite related. So, for those of you familiar with the chemistry of spinels, these are four anions, right? The base unit of spinel. But if you look at it, we actually have about almost 3.3 cations. So, we have more cations, normally have three cations for four anions in a spinel. So, we have more. These metals can today not be made by classic solid-state. They have to be made by ball milling, which is a disadvantage of them. But we think we have ways that we can get to these with solid state reaction. And first of all, they have very high capacity. They have a much smoother voltage profile. It still has some features in it. But we can now get over 300 million A hour per gram capacity. Our discharge energy is over a 1000 watt-hour per kilogram at a sort of respectable voltage. But we also have good capacity retention, although capacity degrades at high voltage. And I will say something about that in the end. But here's the shocker. So, when we make additional electrodes, we can discharge at a 1000 mA-hour per gram, even at 2 amperes per gram. When we start to improve the carbon content of the electrodes by adding more carbon, by optimizing the electron transport, we can even do discharge it up to 20 amps per gram. So, even higher than any other DRX material or spinel material that we've seen. And that actually is because of the excess cation content we have in the material. So, this material is actually starting to look a lot kinetically like the lithium titinate anode, which is also super high rate.

So, I want to end with a few slides and one is about cost. And again, this has been brought up. Lithium ion batteries have become quite inexpensive. And when they were a thousand dollars a kilowatt hour, then the cost of the metals didn't matter. But today, lithium ion is one hundred dollars per kilowatt hour at the cell level and a significant amount of that is starting to become the metals cost. Just to refresh this, I looked up the metal price yesterday. This is the spot price, though. Cobalt is at $47 a kilogram. Nickel is at $18 a kilogram. And this is actually the trend of nickel over the last five years. While there's obviously a lot of fluctuation (this is in dollars per pound, not per kilogram), there is clearly an uptrend here. Right. DRX materials, on the other hand, will enable us to use very simple precursors. Some of the most promising DRX materials are based on manganese as the redox development and titanium as the stabilizer. And both these metals come in precursor that are less than a dollar per kilogram metal content. So, imagine, right, that lithium ion can be low cost. Professor Whittingham already alluded to this, right? So, lithium ion today is really, really good. That's one thing. It is produced in high volume. It is reliable. Imagine that instead of one hundred dollars, it's fifty dollars a kilowatt hour. I think you would see basically all energy storage go towards lithium ion.

So, what are the challenges left to deal with DRX materials? We can do very stable cycling. We can go up to 4.4 Volt. But to unlock the very high energy densities, you need higher charge voltage. And we are quite certain at this point that the materials are quite stable. But we see significant electrolyte breakdown at these high voltages and at least products on the cathode would lead to increased polarization. It also leads to some shuttling of products to the anode which destroy the anode. So, we really need to work on surface protection on novel electrolytes for these materials. They also have a wider voltage range than some of the DRX materials. So, some of DRX materials need a larger screen of charge and discharge voltage.

But let me end here with the conclusions that we have to worry about resources and DRX materials give us a pathway into using other different metals. It's a very large design space. We can use almost any metal you want to, which, like I said, there's a lot left to do here. We can definitely activate double redox of manganese, which is quite exciting. We use titanium as a stabilizer, which is low cost. I think we have now seen multiple strategies in the literature, some from our team, some from others that you can do high rate with some of the new DRX chemistries. And I'm very excited about this here that fluorinated DRX materials team seem to have very high stability against oxygen loss. There seems to be very little evidence of materials being done. And I think I'll sort of end with that, that we have seen in extreme cases, specific energies as high at a 1000 watt-hour per kilogram. And then at the end, I want to thank the whole team, which is certainly my own group. But this is also a very broad collaboration between many national labs and UC Santa Barbara as part of the Low Cobalt and Low Nickel Program of the Department of Energy. So, thank you for your attention.

Discussion

현택환:

Thank you very much, Professor Ceder, for the wonderful presentation. Now let's move on to the discussion session. And Professor Whittingham, welcome back. And today we have four speakers and Professor Kisuk Kang and Professor Jang Wook Choi will join us here and Professor Ceder and Professor Whittingham will join via Zoom. OK. All right. So, let's begin the first question. So, as you may know, South Korea played a central role for the last several years in the battery business. And in terms of global market share, actually the dramatic increase compared to 2019, 16 percent market share in the battery market, it rose to like 35 percent last year, 2020. So, obviously playing a central role in the battery area. So obviously, the next generation battery will play a game changer to revolutionize the current battery market. So, my question is that what must industry, academia and government should do to play and continue even more central role in the battery business. So, Professor Whittingham, would you go first?

Stanley WHITTINGHAM:

Yeah, clearly one area where the field is trending is to safer systems. And safer systems might involve finding a totally new liquid electrolyte. We've used the same one for 30 years. Maybe we can change that. But I think also the key area people want to work on is solid-state batteries, as a lot of effort, I would say in academia in the US, is doing that. Toyota is clearly working on that. But the key there is a solid-state and pseudo-solid-state. And I mentioned the loose solutions, polyethylene oxide solid-state batteries, those are true solid-state, but if you talk to folks making these ceramic based electrolytes, always ask them how many drops of liquid you add to your cathode and they will invariably tell you they have to add liquid to basically grease that interface so you can get high rate diffusion between the electrolyte and the cathode. But equally important to get ions to to diffuse between one cathode particle and the next one. So, it's a tough area. I haven't heard much come out of South Korea on that. But I suspect most of your industry is working on it quietly in the background. But I know for ceramic solid-state, I still think it's 5 to 10 years down the road. Whether the French can get polyethylene oxides to work at room temperature, you know, that would be a breakthrough, but if you're talking large commercial applications, fleet vehicles, it may well be advantageous to work at 50 or 60 degrees as they do, because then you do not need thermal control and even on systems that might operate at room temperature if they get higher in temperature, it will not damage the system. That's another advantage of solid-state. I think, my thing is that's where the future is probably going to be. We're talking about extremely high energy densities, it's probably lithium sulfur. A lot of people have been working on that for 50 plus years and some really serious issues there. And I suspect we're going to need solid-state electrolyte to make lithium sulfur cells work. But in the end, it needs academia, national labs and the industry to all work together and bring all the different disciplines together to make a breakthrough in some of the areas.

현택환:

Thank you very much. Actually, by the way, more than two thousand three hundred people registered for this webinar. It is a tremendous number, and actually we received more than 450 questions from the audience. All right, Professor Ceder, could you add to the question I asked earlier on the role of the academia, industry and the government?

Gerbrand CEDER:

Yeah, thank you. Yeah. Let me add to what Professor Willingham said, that I think battery is an applied field and we sometimes focus a lot on performance, but I think when you build an application, you don't always know what skills you will need, where new invention will come from. So, I think government should keep a keen support for the basic chemistry, physics and science that enables batteries. I think you've got a great example that, you know, when Professor Whittingham was working on TiS_2, people were working on these chalcogenides for superconductivity at the time. We would have never figured out how these DRX cathodes worked if we hadn't spent 15 years before time on understanding the basics of the fusion. And we wouldn't have been able to make predictions about materials if people in the 1970s and 80s had not figured out how to do computational quantum mechanics.

So, I think we have to keep in mind that that batteries require a lot of diverse skills and we should pull these in as needed. For example, in solid-state batteries today, you obviously need people with very good knowledge in mechanics because these are solids now that have to fit together and deform, and this is not something we have traditionally done. So, I would say that's one thing is try to motivate people with good basic science skills to enter this field.

I think the other one is long-term support. You know, this is a long haul to make better batteries. It's been successful, but Rome was not built in one day. And I think you have to let people pursue new directions, not just “What's your performance tomorrow?”, but figure out what goes on in materials, understand why some materials work and why some details don't work. Because I feel every time we understand why something does not work, I think we also get better at understanding how we can make things work. And I think that my experience is that industry in Korea is very receptive to that, that there's a significant, serious appreciation for kind of basic science from industry in Korea. So, I think government should stimulate that collaboration even further.

현택확:

All right, thank you, professor. Professor Kang, do you have something to add on that?

강기석:

Ok, if I add a little on what they have said, I think it's quite natural that technologies compete each other. And I think the industry should be always ready to adopt this emergence of the new technology or alternative technology. And I often compare this battery field to the semiconductor field, and we know that now the silicon technology dominates over non-silicon, like the III-V compounds. Even though there are some demerits of using III-V compounds, still silicon technology dominates. And it is because of the massive production and massive investment, which leads to the new findings over and over. OK, and this also gives the competence with respect to the cost.

I think there will be some point in the future that this post-lithium-ion battery technology, including sodium or lithium air or solid-state battery, will become sufficiently mature to compete with that of the lithium-ion batteries. So, in that respect, I think the industry part should always keep track of the recent progress of these ones. And there are several metrics that determine the battery performance, like energy density, cycle life, safety, power. And the currently lithium-ion batteries actually excel in almost all aspects of these over post-lithium-ion batteries. But if you normalize these properties per cost, in the future, we don't know which is going to be dominant. I think, as Professor Whittingham said in his presentation that if the energy density is the only matter, then those post-lithium-ion batteries are not going to work and the lithium-ion battery is going to dominate. But if there will be some applications beyond electric vehicles, then I think there will be some rooms for these post-lithium-ion batteries. In the case, we are currently fortunate that our Korean companies are leading this battery field. SK, LG and Samsung are doing very good. But if the are changed, then I think there would be some risk. So, in the respect, industries have to focus and they have to develop their own capability to address these future challenges. And at the same time, academia, I think, are supported by the government and industry have to focus more research on the fundamental sciences on this post-lithium-ion battery so that we can, in the future also, lead this energy storage field.

현택환:

Thank you, Professor Kang, Professor Choi, would you add something?

최장욱:

I think I think I'd add a bit more. I think all other three speakers already covered pretty much all about the material and cell perspective. But I like to just add other parts in academics who could contribute a lot to the better technology, which is a computer science and electrical engineers. Because beyond just material discovery and cell optimization, also, we better be concerned about how we operate the cell, you know, in an intelligent and smart manner. So, sometimes we better communicate with our users to operate a cell in a more optimized manner. So, I think in that sense, we could be concerned about how we develop BMS using better algorithms, better sensor technologies, and better circuit technologies. And with all these combined together, I think we could expect better batteries. Thank you.

현택환:

Thank you very much, Professor Choi. And let's move on to the second question. Following the large-scale integration of energy storage system, ESS, in Korea, a lot of news came out on fire accidents. So, this is inevitable. With increased battery performance and energy density, higher risk of fire and explosion is inevitable. So, in academia especially, what kind of research shall we do to overcome, prevent fire and explosion and develop non-flammable battery materials and address that kind of safety issues? So, Professor Kang, do you want to go first?

강기석:

Ok, well, the battery can explode when three conditions are met. If there is fuel, oxygen, and ignition. Inside the battery, we have organic electrolyte, which can serve as fuel and we have oxides, cathodes, which can also serve as oxygen source. And if you have some additional external shock or physical or mechanical or other kind of the factors, then there can be some chances that ignition can occur. So, regarding the safety of the battery, it is quite natural that if the battery or in general, energy storage system, has a higher energy density per volume in a given space. Naturally, there are more risk of safety. It is like if you deal with nuclear power, then the consequence of the safety issues is going to be disastrous. And for the low energy density battery, if there is a safety concerns, then it's going to lead to the small safety risk. So, when we talk about the higher energy, higher energy and higher energy density batteries, we always go with taking a higher risk for safety. The most important thing is how we can kind of control these safety issues of the battery.

So, I can divide the safety of the battery in three different levels. So, number one level is the material safety. So, all the materials inside the battery should be tolerant and that they should be safe. And the second level is the cell itself. When these components or battery materials are assembled in one cell, and if there is some mismatch of these materials and if something's happening inside cells, it's going to lead to safety.

And the top level is going to be the system level of the safety. So, when we use the batteries in electric vehicles, we have about, for example in the Tesla, 7,000 cylindrical cells are connected in assembly in one car. So, if these cell balances of each cell are not properly done, some of the cells will be overcharged and some of the cells is going to have high resistance. So, it's going to lead to safety incidents. So, in the top level, we have to focus more on how we can manage different cell conditions, those kinds of things. And fundamentally, the most important issue is how we can make the chemistry itself in the materials level safer. So, there are many researches going on now. As I said, the electrolyte, an organic solvent, is the main source of the fire, fuel. So, there is a trend to move to the solid-state electrolyte. Of course. I mean, the ceramics are not are not flammable, so the uses or replacement with the solid electrolyte is going to be the one solution. And also, another solution is to regulate the oxygen sources from the cathode as Professor Whittingham and Professor Gerbrand Ceder talked. The oxygen evolution from the cathode can be inhibited by changing to the phosphate chemistry or fluorine chemistry. So, those kinds of regulating oxygen can also be one of the possible ways. Also, we can go to the other totally different electrolyte system, like using a retardant solvent. Rather than flammable, we can switch to inflammable solvent electrolyte system. So, by having high concentration concept, high concentration salts those kinds of concepts have been demonstrated in recent years. So, we have to systematically approach these safety levels, which have to be taken care of systematically in different three levels.

현택환:

Thank you. Professor Choi, do you have something to add on that safety issue of the battery?

최장욱:

I think, Professor Kang already mentioned about three different levels, but I’d like to add a manufacturing viewpoint. Most fire hazards usually come from defective cells. Then the question is how we avoid them. I think our current industry actually evolved quite a bit to adopt advanced technology in terms of smart manufacturing to diagnose some defective cells in earlier stages. I think with such manufacturing technology, I think we could predict better opportunity to avoid this fire hazard.

현택환:

Professor Whittingham, Professor Ceder, do you have something to add on this safety issue?

Stanley WHITTINGHAM:

Maybe very briefly. We learn by our mistakes, I think. So, now we have these battery problems with the 787 plane, and that was in the end a design issue. The sensors were in the wrong place. Fire could propagate from one cell to the next one. I think they've overcome a lot of that now. So, I think we have to pass the message if something goes wrong, let everybody know.

And I think the other thing we learned, and I think it was an LG storage system that injured about 6 firefighters in Phoenix, Arizona, maybe two years ago. And the case there was no one had trained the firefighters as to what to do and specifically what not to do. So, we've had a number of systems set up in New York State. And I've taught some of the firefighting chiefs and they trained every firefighter how to handle a battery fire. That's going to become more and more important, as we get more batteries in cars and other devices. But I remind everybody that if you were to invent the internal combustion engine today and you say you are going to put 20 gallons of gasoline under the back seat and sit a two-year-old on top of it, you will not be allowed to do it. So, we have to put everything into perspective.

현택환:

All right, thank you. Let's move on to the third question. In terms of different kind of energy devices, solar cells. Solar cells are another renewable energy source. Pretty much every day, day by day, in the National Renewable Energy Laboratory in the United States, there is a chart. And, you know, the number for the solar cell efficiency goes up and up day by day. So, now let's talk about the battery, rechargeable battery. What's going to be the limit of the battery efficiency? How close are we to that kind of limit of the battery capacity? Professor Ceder, please.

Gerbrand CEDER:

So, I think within the lithium-ion, there's definitely still some room to grow. You saw, you know, Professor Whittingham show how you might get rid of the irreversible first capacity. We might be able to go to new cathodes. If silicon , there will be an increase in energy density. So, there's definitely room to go in the lithium-ion. And keep in mind, the industry has done a fantastic job of improving energy content small bits at a time. But as I always say, you know, if you do 5 percent each year over 10 years, that's actually a lot. So that's one thing I would say.

I do think, though, that solid-state has the potential to move us to a new plateau, to a new development curve. You know, maybe lithium-ion will end up at, you know, maybe we will someday make 800-900, maybe 1,000Wh per liter. Solid-state today is definitely not there. But the fact if we can use lithium metal or even go anodeless where the lithium metal is all deposited from the cathodes, so you don't even have to work with lithium foil, I wouldn't be surprised that by the time I retire, we can do 1,400-1,500Wh per liter. Because if you look at sort of best-case scenarios of cell models, these are not impossible. I'm not saying today. People will probably vilify me if I say we're going to do that today or tomorrow. But if you take the development curve of lithium ion where it was 20 years ago and where it is today, and if you now imagine sort of systematic improvements in solid-state, we might actually double energy density from today in the long term. And I'll hope I'll see that before I retire.

현택환:

All right. Thank you. You already brought up, I think, question number 6, which is about the all-solid-state battery. So, this is one of the buzzwords, the most important word in the battery industry and also in academia, certainly. What shall we do to actually make this all-solid-state battery feasible? What kind of limitations are we facing now and what shall we do to overcome that kind of limitations to have all- solid-state battery? Anybody have any comment?

Gerbrand CEDER:

Well, let me start and I'm sure other people will chime in, I think. First of all, I think we have to realize that solid-state is still in its infancy. It is still very early for solid-state. I know that everybody wants to claim to have a great product. But we are really at the very early stage of solid-state. In my opinion, we need both better materials, we need better manufacturing, we need to understand the long-term behavior of lithium metal better. I think on the material side, I feel like we are trying to run before we can walk. We have essentially two or three good solid-state lithium-ion conductors and industry is trying to run with that. These materials are not very good when you look at it there. In the end, not very stable. Their conductivity is OK, but not great. Many of them are highly reactive. So, I think we need better conductors and that's definitely feasible. A highly stable, high-conductivity material is definitely possible. We need to have creative ideas on how we integrate all-solid-state materials together without adding liquids and plasticizers, and so like Professor Whittingham hinted at. And that's obviously done a lot. But these things are possible. And then of course, there's lithium metal, which will always be a challenge, will always come with potential safety issues. I think we have a lot to learn about how lithium metal plates, what its reactivity is with solids, how it can penetrate solids, which it does in some scenarios. But again, let's not forget, it is a very early stage. Right. Maybe this is the titanium sulfide days of solid state. Maybe I’ll put it that way. We have a long way to go on solid-state. So, let's not forget that.

현택환:

Professor Ceder, this might be a provocative question to you, or all three of you. So, can we really have that kind of all-solid-state battery within ten years? Is it going to be possible with pretty high

Gerbrand CEDER:

I’ll let my colleagues answer that first. I'm going to see what they say.

현택환:

Alright. Professor Whittingham?

Stanley WHITTINGHAM:

Let me add a comment. Remember, we do have a commercial all-solid-state battery out in the market today. And that’s the one with PEO (polyethylene oxide). It operates at 60°C. I don't know what its energy density is. I suspect not all that great, but we have it now. I'm hoping we all learn by the pluses and minuses of that system. We can then apply it to others.

And remember, when I got in this field, I went to Stanford in about 1968, 70. The interest then was could we make a solid battery using beta alumina as a solid electrolyte. It had just been discovered and Ford Motor Company was going to build batteries using it. So, the challenge there was we didn't think we could understand the interfaces—that’s still a challenge today. So, the intent then was to use molten sodium and molten sulfur and have a solid electrolyte in between. So, I think the next step we might see if we get a good, solid electrolyte is a lithium solid electrolyte sulfur cell before we actually go to three components all solids, because you could have real interface issues. We don't even understand those in today's batteries.

현택환:

All right, thank you. Professor Kang, do you have something to add to that?

강기석:

Yeah, maybe if I add, we agree that there is a huge driving force now moving toward all-solid-state batteries. It is clearly because of the two important factors. One, safety is almost guaranteed because the fuel is gone now. And the second is the volumetric energy density and form factor. So, if we replace this liquid type of electrolyte with a solid type, then we don't have to worry about the sealing of the cells or the shape of the cell. Currently, the lithium-ion battery has to contain the liquid type of components inside. So, we have to deal with how we’re going to seal it and what's going to be the shape of the battery itself. But when we change to the solid-state materials, then various kinds of process engineering can be easily adopted to a new level. We can change the battery shape from typical cylindrical to any kind of shape. So, when we think about how we’re going to load this battery onto the applications, electric vehicles, we can change the battery shape in any kind of things. Or in other future applications, there are clearly advantages on that. But we also agree that there are clear challenges, grand challenges in achieving those goals. One of them is the interface problem. We all agree with that. By changing from the liquid-to-solid interface in the conventional battery to the solid-to-solid interface, a totally different story, you have to ensure that all the solid-to-solid interfaces are in contact throughout the charge and discharge of the battery. Once you use the liquid, this liquid form naturally covers all the changing shape of a particle, but now you're going to have irreversibly contact loss of the interfaces. So, how are we going to deal with this interface is going to be a key problem in the future, I think, for the future of the solid-state battery.

And also, regarding the specific energy density, specific energy, which is density per mass, weight, there are demerits of using the solid electrolyte. You need only a drop, a few drops, of liquid electrolyte to wet this electrode to function in the conventional lithium-ion battery. But you need to have a large portion of the volume to fill the space between an electrode material and an electrode material of by the solid electrolyte. So, it inevitably accompanies the increase in the weight of the cell leading to the loss of the energy density. So, it's going to be another factor that we have to consider. That is why using conventional anode material is not going to offer merits in the energy density or the solid-state battery driving force. That's why we have to move to the lithium metal, which can offer much higher energy density. So, lithium metal in the solid-state electrolyte should be matched with the lithium metal to compete with the energy density of the current lithium-ion batteries. And it also causes new stages of problem as well. So there is a long way to go, but there is a clear driving force for that.

현택환:

All right. Professor Choi, could you add something more on that?

최장욱:

I mean, since Professor Ceder tossed answering the feasibility of the technology, maybe my answer: in the next five years, it is very difficult, but maybe in the next 10 years, I would bet on the positive side. I mean, beyond all the materials and seal perspective and energy density perspective, I'd like to add the importance of manufacturing, because now we may have to have different electrode compositions compared to the current lithium-ion batteries. We may have to start designing the manufacturing from the scratch. Maybe we better choose the drying process instead of the solution-based process that the current lithium-ion battery industry adopts. Of course, we need to see what the economics of manufacturing process will be. And of course, in the end, we need to worry about energy density per dollar, and also the lithium-ion battery will continue to evolve to deal with all these safety issues. So, in the end, 10 years later, I don't know which one will be above than the other. But still, people are smart. And as Professor Kang mentioned, there is a huge driving force. So, I think in the next 10 years, I think I would bet on the positive part of the technology.

현택환:

All right, thank you very much, Professor Choi. Let's move on to the next issue. Battery use increases tremendously for, not just laptop computers, cell phones, but now electric vehicles, a lot of different kind of applications. As Professor Ceder mentioned during his presentation, we are running out of resources. So, lithium and cobalt, and this kind of materials is running out. And I guess now it's time to think about what shall we do? What shall we do to develop sustainable battery technology, such as reuse, recycling, and also recyclable battery service. So, what do you think about this issue of sustainability?

Stanley WHITTINGHAM:

It has to happen.

현택환:

Oh, yeah. Professor Whittingham. Why don't you start then.

Stanley WHITTINGHAM:

I think the issue is here. There is, clearly in my mind, a real chance that cobalt is going to have to go. Cobalt is also the most valuable material in the battery, so once it's gone, there's less value in recycling. So, I think just like today in the United States, you have to recycle your lead acid batteries. And in Europe, the manufacturer has to be willing to take back your car. So, in the end, the politicians are going to mandate that we have to recycle all these batteries. And I know the small ones in computers and smart phones, I understand 80 percent of them are not recycled. So, we probably got rather rich cobalt deposits in some of our garbage dumps. I think all of that has to be recycled. A number of facilities are now being built in the United States to do exactly that. There was, in fact, a South Korean company trying to build a recycling facility in the old IBM facility just four miles from me. And it looks like a much larger effort is being built by a Canadian company in Rochester, New York, in the old Kodak facilities. So, they're going to do the recycling there. One of the challenges in recycling large batteries is they are considered hazardous cargo. So, more than the third of the cost of recycling batteries is actually taking the batteries to the recycling facility. And discussion I had, I think it was yesterday, on this. An easy way around this apparently is you recycle the whole car to take the car to recycling facility. It is not a hazardous material then until you take it out of the car. So, you'll actually be recycling the cars at the same place that you're recycling the batteries. And maybe the same with other devices. In the end, it is going to be a political decision. I'm sure places like South Korea and Europe are far more advanced than the U.S. in insisting that everything gets recycled and reused. We can't afford to keep digging up more and more material. And I know there's been studies by the Department of Energy here that has shown within about 15 years, more than half the lithium going into new batteries will come out of old batteries and will have less demand on the raw materials. So, it has to happen. As I said, to make a 1KWh battery, it takes 60 to 80KWh of energy, so we have to find sustainable ways of recycling batteries and don't use all that energy all over again.

현택환:

All right. Thank you, Professor Whittingham. Professor Ceder, do you have something to talk about reuse, recycling and sustainable battery technology?

Gerbrand CEDER:

Yeah, so I, I agree that it has to happen. Right. This is my worry is when it will happen, because in the end, recycling is in part an economic issue unless you mandate it. And the economics is not good. Right. So, when you sell your fancy Tesla after, let's say, 10 years, the battery still actually has a very good performance. All the data coming back is showing that even after 10 years lifetime, we see large battery packs with 85, 90 percent or more of their capacity. So, the question is, this is a battery pack that costs, let's say, ten thousand dollars to make, a round number. Recycling. The value of recycling today is about zero because there's cost for shipping it, there’s cost for dealing with it. So, the question is who will give their battery away if it's actually still so valuable? So, my worry is that if we wait for the recycling stream of minerals to come back, we're going to have to wait a very long time because batteries are going to stay in circulation, I think longer than expected. They will have second use. Let's say I'm a Professor Ceder, a battery recycler. I will sell you used energy storage for twenty dollars a KWh so you can get something that's 90 percent good for twenty dollars from me instead of going to LG or Samsung and pay a hundred dollars a KWh. I think there will be a lot of uses for this. And Elsa Olivetti at MIT and I studied this quite extensively. What that means is that the recycling stream, what is made today, it may take 15 or 20 years to come back. That means we're going to have 20 years of enormous mineral consumption, whether it's lithium or nickel or cobalt or whatever we actually end up using. Right. So, I know that governments like to point out recycling as their way out of the resource problem. But if you're going to make 5TWh in 2030, recycling will contribute about zero to that mineral content. That's the real problem.

현택환:

All right. Thank you. Professor Kang?

강기석:

Ok, I agree, I mean, everybody agrees that recycling and reuse of the battery is going to be very important matter in the future, but economically speaking, it’s not an immediate challenge right now because people in industry, they are trying to get higher energy density with a high-quality battery. But if you look at the trend of electric vehicle market penetration, if you calculate the number of batteries that are produced every year and if we add up 10 years or 20 years of market penetration, it is going to be a huge volume of the battery. So it's going to be not only the issue of the economy, it's going to be also the issue of the environments. We're going to have a pile of batteries facing to be wasted. So, we have to think about how are we going to deal with it. In fact, academia is now beginning to address these issues. One of the approaches is to develop the material that can be more sustainable without any use of transition metal. So, there is a field of organic-based batteries which do not completely use this kind of transition metal, which can be scarce. And also, there are studies on how we can reuse the cell. The batteries that have been retired from electric vehicles still have a certain level of performance. And there are some applications that they still need those applications at a lower cost. So how are you going to make a transition from this one application to the other? And this is actually one important research area. And one of the other things is that some researchers, including me, are trying to develop biodegradable batteries. So, when there are a lot of piles of batteries, just like plastic bags, we have to think about how we are going to deal with it?

현택환:

All right. So, Professor Choi, do you have something to add on that?

최장욱:

Focusing on the reuse of the batteries, I think one of the immediate technologies required is how we evaluate the state of health. For example, I have some use of batteries, if I want to sell, sell them to somebody, then I need to convince them. If you buy this one, you can use this battery at least for five years with a certain state. Then, how do I quantify the state of my batteries? I think we need to quantify the state of a battery in many different perspectives, so that there could be some natural economic platform people could easily build trust on. for all the sales. I think that technology is something, I think, is one of the high emergency to really operate this reused battery market.

현택환:

So, let’s move on to the next question. Now, not only are batteries used in mobile devices, like cell phones and laptop computers, but also most importantly in electric vehicles. So, there is a lot of new emerging markets using batteries such as urban area mobility (UAM) and even airplanes and ships and trains. So, to use batteries for these kinds of new emerging areas, what kinds of challenges do we have and what shall we do to overcome those kinds of challenges? So, anybody has any opinion?

Gerbrand CEDER:

I think that's a challenge we have. I think Professor Kang already hinted at this. There are in principle other good energy storage technologies, electrochemical, sodium or lithium sulfur, and even solid-state. And in some of these applications, these technologies might in principle even be better. It might be more cost effective, for example. But the problem with bringing a new technology to market is that even things that should be inexpensive in principle are rarely inexpensive on day one. So, a successful technology typically has an entry point into the market that's very high value. And for solid-state, for example, we can see that, right. Solid-state probably will have an entry point in phones, portable electronics, where the value is high and the phone makers will pay more money. And then you can sort of trickle down the cost and come out of it and you can go everywhere else. The problem with many other technologies, say flow batteries or sodium-ion is that while they are inherently better in doing some things, they don't have a good high value entry point in the market. And I think that's in part why it's been difficult for industry to support them, because they have all these development costs and they don't have a high value application that they can get the costs out. And this is why the incumbent technology is always so hard to beat. We see now it's silicon in the semiconductor industry, right. Even though there are other semiconductors, which maybe in principle are better, we still use silicon and lithium-ion is now the incumbent. Lithium-ion with NMC or LFP is basically incumbent and it's hard to beat.

현택환:

Thank you. All right. I think time is running out. Let's move to the last question, which is specifically to Professor Whittingham. So, you received the Nobel Prize in Chemistry 2019. And as I told you, more than 2,300 people registered for the webinar and among them there is a quite a lot of Korean youngsters here. So, when you wake up in the morning, what makes you so excited, “I have a new great day.” What makes you think that kind of stuff? What is your motivation? To encourage the youngsters, please.

Stanley WHITTINGHAM:

I like challenges, I like changes. And I should point out, I started in industry. I worked on batteries for maybe 10 years, and then the way Exxon works, I went into management and I became a division manager of chemical engineering, looking at syn-fuels and things like that. And I decided that didn’t excite me. So, I moved to academia. One reason to go into academia, new, young faces each year. So, the young people keep you young as well. So, I'm excited about interacting with younger folks. I always tell them, “Only do things that you're excited about doing. Don't do things for the money because in the end you can be unhappy. And take on challenges and not everybody's going to like doing research. Learn it quick before you spend five years on PhD and say, I hate doing this. But do things that excite you and that you love doing.” This last year has been has been tough because I can't interact with the students face to face.

현택환:

Thank you very much. All right. Thank you very much all for the wonderful discussions, especially Professor Whittingham and Professor Ceder for joining late at night, Eastern Time Standard, and also late in the afternoon, Professor Ceder. Also

Professor Kisuk Kang and Professor Jang Wook Choi for joining in the wonderful discussion. Thank you very much, all of you. Thank you.

Keynote Session

All right. Let's move on to the third presentation by Professor Kisuk Kang. Professor Kisuk Kang is a Professor of Material Science and Engineering at Seoul National University, and also he has been serving for the last couple of years as Associate Dean of College of Engineering at Seoul National University. He received Bachelor’s from SNU, and he actually did PhD with somebody here, Professor Gerbrand Ceder when he was at MIT. And then, he first got his position at KAIST and moved to SNU in 2011. And he is, not rising, already a risen star in the material science area. And he has been doing first in computational science to design new materials, especially for batteries, and not only design but also experimentally developing new materials for batteries. And he published many papers, and the last couple of years, he was selected as a highly cited researcher by Clarivate Analytics. Today, he will talk about “the New Battery Chemistry from Conventional Layered Cathode Material for Advanced Lithium-Ion Batteries.” Professor Kang, please.

강기석:

Thank you for the introduction. I'm very happy to participate in this workshop and hope that this is going to be a good opportunity for us to communicate regarding the state-of-the-art lithium battery technology. I think now the presentation is going to become a little bit more technical. We are going into the real science, now.

So, the title of my talk is “the New Battery Chemistry from Conventional Layered Cathode Materials for Advanced Lithium-Ion Batteries.” In this presentation, I will talk about how we can take a full advantage of the layered transition metal oxide as the cathode, which has been discussed by Professor Stanley Whittingham and Professor Gerbrand Ceder, and has been the dominant cathode material for the current lithium-ion batteries. In the previous talk by Professor Stanley Whittingham, it was very well introduced how the mono-lithium-ion battery has been shaped, which was primarily thanks to the discovery of the layered intercalation compounds, allowing the highly reversible lithium insertion and de-insertion. So, the current limitation in achieving a higher energy density battery lies in how we can gain more lithium and electrons from the electrode without jeopardizing the stability of the electrode materials. So, in this respect, I will discuss about our new findings on the layered transition metal oxide. When more lithium ions are stored by the additional redox reaction through the oxygen redox activity, which is so-called lithium excess layered transition metal oxide. So, I will show that the lithium intercalation mechanisms are significantly different in these materials and this is correlated with various stability problems of these materials. So, based on this understanding, we developed a new layered lithium excess transition metal oxide that can circumvent these problems. And I will present these results today.

Just for recap lithium-ion batteries are composed of three major components, the cathode, the anode and the electrolyte. So, with charge and discharge of the battery, lithium ions are extracted from one electrode and reinserted to the other. This is actually the crystal structure of the layered transition metal oxides we have seen in the previous two talks. And one thing that needs to be reminded is that on the cathode side, which requires a high redox potential, the redox reaction relies on the oxidation and reduction of this transition metal, in this case, cobalt, which allows electron storage. So, the transition metal redox activity exhibits generally high potential and the high reversibility. And this is actually why most of the cathode materials contain these transition metals, such as lithium cobalt oxides, NCM, lithium iron phosphates, and lithium manganese oxides. They all have transition metal in it because of these reasons.

One of the interesting findings in recent years was that not only the transition metal here, but also the oxygen in this overall material can participate in the overall redox reaction at certain circumstances, offering additional room for capacity. In conventional cathodes like this, the capacity is provided by the redox of transition metal and the typical capacities of about 140 to about 200 mA/g at the best. But when the anionic redox reaction, oxygen redox reaction is additionally allowed, then we have more size for electron storage, simply speaking. Thus, the capacity can be much more enhanced. In a very simple picture, it is a transition from these redox reactions solely occurring at the transition metal to this cumulative redox reaction from both transition metal and the oxygen so that we can store more lithium and more elections.

So there have been heated discussions on what can make these anionic redox reactions possible and how these can be stabilized. I'm not going to go into the technical details of these discussions, but one of the consensuses and the simple explanation was that when the local environment of oxygen in the conventional layered structure like this, shifts from this in the conventional layer, which has three transition metal above and three lithium below, to this with additional lithium in its surroundings, instead of the traditional metal.

This particular oxygen generates a new state in the density of the states and allows additional and accessible capacity. So, this kind of a local oxygen environment is typically made in the lithium excess material, which has some portion of lithium occupying this transition metal so that these oxygens will have lithium oxygen in the lithium local environment. So, this mechanism was first proposed by Professor Gerbrand Ceder. Despite this promise for a higher energy density, due to this additional anion redox reaction in this lithium excess material, there have been several chronic problems that need to be resolved. And one of them was the gradual voltage decay, which is typically observed when the lithium excess material is recycled as an electrode multiple times. It suffers from user capacity fading over cycles, but also the voltage fading over cycles. Considering the energy density is the product of the voltage and the capacity, the decay of both values makes the energy density decay double. So, regarding the voltage decay phenomena, our group previously reported that it is correlated somehow with a local phase transition from pristine layered structure to this disordered or spinel-like structure. And we suspected that in might cause a unwanted change in the redox reaction. So, inspired by this finding, we hypothesized that the decay of the voltage is partly induced by the structural transition and the activation of the low potential redox reactions. So, taking one of the representative lithium excess materials here, which is lithium 1.2, nickel 0.2, manganese 0.6, oxygen 2, which has about 20 percent of lithium occupying the transition metal layer. Therefore, the anion redox reaction is possible. We envision that the redox reaction is going to take place like this. So first, during the charging, when lithium is extracted from here, the electrons are extracted from the nickel cation redox reaction contributing 0.4 elections while remaining 0.8 lithium ions are de-intercalated with this oxygen oxidation. And in an ideally reversible situation, the discharge reaction is going to be the exactly the opposite reaction.

On the other hand, if there is a loss of oxygen like this during the charge, the oxygen stays really partially lost, so that the density of oxygen is going to reduce like this. So, during the discharge reaction where we reinsert electrons, some of the originally unoccupied states like manganese will participate in the reaction. So, this will involve manganese 4+ to manganese 3+ reduction. And it is very well known that the manganese 3+, 4+ redox reaction is low in the potential and typically triggers the formation of a spinel-like structure.

So, if this is the case, we thought that we can simply detour this problem by introducing additional empty states here of high redox transition metal in the density of states. For example, if we increase the nickel content from 0.2 to 0.4 here, then the overall oxidation state of nickel becomes 3+, and it will generate the empty state of nickel 2+ just below the manganese states. And even when there is a loss of oxygen during the charge and some of the unoccupied states are going to be occupied by this redox buffer and it will prevent this manganese redox participation, and we call this additional state as the redox buffer.

So, having this simple idea in mind, we designed three samples with slightly different compositions of nickel and manganese, having the same amount of lithium excess in the layered structure. The X-ray diffraction and neutron diffraction from the all three samples were successfully formed in the layered structure, and the X-ray absorption spectroscopy also verified that the samples have the oxidation states as we intended. Interestingly, we found that this simple tuning actually works good in suppressing the voltage decay. As you can see here, the original sample shows the gradual decay of voltage with cycles and is more clearly displayed in this differential curve. So, the voltage was originally about 3.5V, but it reduces to 3V after 40 cycles. But as we add more redox buffer of nickel here, the voltage decay behavior is significantly mitigated.

So, after the cycles, we analyzed the samples to see how the formation of the disordered or spinel-like structures was affected by the presence of the redox buffer, and these experiments actually confirmed that the phase transition was also substantially inhibited with the redox buffer. And finally, we wanted to verify whether this redox buffer concept really works in suppressing the voltage decay. So, the investigation of oxidation states of each sample clearly shows that the original sample with the manganese 4+ and nickel 2+ produces mainly manganese 3+. On the other hand, the sample with the redox buffer shows that even after the cycles, manganese 3+ is not produced. Instead, the nickel was reduced 2+ serving as a redox buffer. So, we clearly demonstrated that the simple change in the composition from here to here actually results in suppressing the chronic problem of this next generation lithium excess layered material. So, we are happy to solve this problem. And it seemed that this new material would be a good high energy density electrode.

But we found that other problem actually emerged with this new material. It showed a comparatively lower power capability. As you can see here, when it is operated at slow charging rate like a C/20, which corresponds to about 20 hours of charging time, it is OK. But when it is charged at a practically important rate like 1C, which is about one hour charging of the battery, its capacity here—the 244 is our sample—is noticeably lower than the usual lithium excess material like the 226. And we found that this low power capability problem is not from the charging process, but from the discharging process. And as we can see here, when we increase the current density during the charge from C/20 to 1C, the reduction of the capacity is not significant. On the other hand, when the same experiment was conducted in the discharge, the capacity reduction is much more appreciable here. And it is a very interesting behavior and has not been observed in conventional layered electrode materials, where the intercalation and deintercalation are regarded as a symmetrically opposite reaction. But this is asymmetric.

So, we could also confirm this asymmetric behavior of sluggish discharge and fast charge reaction here. So first, we discharged the electrode until the normal voltage cutoff and forced further intercalation to achieve 250mA/g. And it naturally exhibits a voltage plateau at 2V, which is reminiscent of the tetrahedral lithium occupation, as we know. And surprisingly, during the charging, this low voltage plateau was not observed and the normal charging curve was observed, which indicates that all the lithium was successfully deintercalated from the octahedral site, not from this tetrahedral site.

So, intrigued by this unexpected observation, we repeated this experiment at a series of other temperatures, but actually confirmed it is reproducible. And more interestingly, it showed that the discharge reaction is much more temperature dependent than the charging reaction. If you look at the low voltage plateau here, it is longest at 10°C, but it almost disappears at 60°C, while the normal discharge capacities recover at this 60°C. It strongly supports that the discharge reaction is asymmetrically more sluggish than the charging reaction. And we found that this asymmetric behavior is actually coupled with the RO-plain transition metal migration in the layered structure. So, this is an atomistic picture of the layered structure, where these bright spots are transition metal and these dark layers are lithium layers. At 60°C, it was found that with charging a significant amount of the metal ions migrate to the lithium layer, as you can see a little bit of bright spots in the lithium layer. But they reversibly migrate back to the original layer during the discharge, recovering the perfect layered structure again. And on the other hand, when operated at room temperature here, the transition metal ions migrate to lithium layers upon charging. But as you can see here, after the discharge to 2V, they do not completely come back. And here we see that the substantial amount of transition metal ions still remains as these bright spots in the lithium layer. But when we forced the lithium intercalation up to 250mA/g, those transition metals are no longer observable in the lithium layer, indicating the recovery of the layered structure. This series of the pictures imply that the lithium intercalation and deintercalation in this lithium excess layered material is strongly coupled with transition metal migration.

According to these observations, we proposed new lithium intercalation and deintercalation mechanisms coupled with transition metal migration in the layered structure. First during the de-lithiation, the transition metal can easily pop up to the vacant lithium layer. And the transition metal migrates back to the transition metal layer during the re-lithiation for normal discharge. But when the transition metal ion in the lithium layer can also migrate here freely in the vacant lithium layer, hopping farther from the original site. And if it happens, it very much complicates the path backward and requires longer migration path during re-lithiation. So, compared with this simple hopping-up of transition metal during charge, this complicated, longer path of transition metal during discharge is believed to result in a particularly sluggish discharge reaction.

I would like to mention that this asymmetrical lithium diffusion is quite contrary to the conventional belief on the lithium intercalation and deintercalation mechanism, which offered Nobel Prize in Chemistry in 2019. In a classical model of the intercalation, the lithium insertion and the de-insertion process should be identical, and the only mobile ions should be the lithium ions. And these asymmetric kinetic properties cannot be explained, as we saw in the previous slides. But our new lithium diffusion model reveals that lithium ion is not the only mobile ions and their motion is actually coupled with transition metal migration. And this involves the reversible but asymmetric transition metal migration, which elucidates our experimental findings. So, the diffusion model in the concept should be rewritten according to our findings.

So, one thing that should be noted is that the transfemoral migration into the lithium layer is thermodynamically favorable at low lithium stoichiometry, and it is an almost unavoidable phenomena during the charging process. And once transition metal in the lithium layer is distracted like this, a much longer migration path awaits during discharge. And this actually results in two consequences in lithium excess material, one with the redox buffer, as we have seen so far, the sluggish kinetics and the low capacity. On the other hand, for the material without the redox buffer, which induces manganese 3+ ions, this transition metal migration triggers a massive phase transition of the materials to a spinel-like phase, causing a significant voltage fade.

Then how do we resolve this? So, if the transition metal migration to the lithium layer is inevitable because of the thermodynamics, we thought that the substantive key to minimize its negative effect is to streamline the structure so that transition metal migration only occurs at this path and inhibit other migration, other path, such as these in-plain migration in the lithium layer. And this will block the further migration of transition metal to here and is going to block the path here.

So then how do we ensure that the transition metals do not go astray in the vacant lithium layer and readily come back to its original site when lithium ions are re-intercalated? We believe that we can control this transition metal migration by altering the stacking sequence of layered structure from conventional O3 structure where oxygens are stacked in the a-b-c-a-b-c stacking, to O2 structure with the a-b-c-b-a stacking. So, they have a little bit different stacking sequences. If you look at closely the local environment during the transition metal migration in each layer of the structure, they are quite different. In the conventional military structure, the transition metal are actually hops to the lithium layer via this intermediate site, tetrahedral site, and jumps to the nearest octahedral site. And these octahedral sites are relatively stable. Therefore, this process can readily occur, making this in-plain detour possible. On the other hand, in the O2 structure, this octahedral site is strongly repulsed by the transition metal underneath. So, the transition metal has no choice but to come back to its intermediate site again. And so, it is locked only on this path. So, this difference in the stability of the octahedral sites arises from the different stacking sequences of oxygen, transition metal, lithium, and transition metal of the O2 and O3 layered structures.

This argument could be supported by our first principles calculations on each site. So, as we can see in the graph showing the relative site energy of the transition metal, it is shown that transition metal in the initial site of the O3 structure can easily go to the intermediate site, and finally ends up in the octahedral site with a negative energy slope. On the other hand, in the O2 structure, the transition metal can hop into the intermediate site, but it cannot further migrate to the neighboring site because of this high energy barrier. So, this theory actually confirms our ideas.

So, inspired by this idea, we decided to synthesize the O2-type lithium excess layer. But unfortunately, we could not obtain the phase using the conventional solid-state reaction and had to go through the indirect method where we prepared the sodium version of the lithium excess material in P2-type layered structure, and ion-exchanged sodium with lithium through soft chemical methods here. And the X-ray diffraction patterns on the left confirmed that we successfully obtained the O2-type of layered structure, lithium excess material, from the P2 type of the sodium phase. And the particle looks like this.

And to our surprise, we found that this O2 structure is very effective in retaining the energy density. This figure presents the first charge, and second charge and discharge curves of the O2 structure, which delivers a capacity of more than 230mA/g. And the vaulted profile of the discharge was almost unchanged over 40 cycles without the decrease of the voltage, indicating the success of our strategy. So, the comparison with the conventional O3-type sample more highlights the stability of our electrodes. Because of the suppressed voltage decay, the retention of the practical energy density of the O2-type lithium excess material was about 83 percent, corresponding to about 600W/kg after 40 cycles, which is actually much better than the O3-type. And we found that the stability in the voltage and the energy density is really attributable to the reversible and the symmetric transition metal migration during charge and discharge, which we really intended to accomplish. And as we can see here, after the charging, transition metal is clearly visible in the lithium layer, which means that the metal migrates to the lithium layer, but they completely disappear upon discharge even at the room temperature operations. And this actually indicates the reversible migration back and forth we intend to achieve.

And this reversible migration of transition metal also prohibits the unnecessary formation of the disordered or spinel-like domains in the structure, as can be seen here from this Raman spectroscopy. And moreover, the structure stability could be maintained even after the long-term cycle. So, we could confirm from the electron diffractions in the system. So, this clearly shows that the very simple modification of stacking sequences of the structure actually prohibited these chronic problems.

So, in summary, we showed that there is still such interesting new chemistry in the layered structure, which requires actually rewriting of the classical view of lithium diffusion or intercalation models. And the proper structural redesigning of the layered structure can further offer us the stable and the higher energy density electrodes for advanced lithium-ion battery.

And with that, I'd like to thank the audience online and my group members and the funding sources. Thank you.

현택환:

Thank you very much, Professor Kang, for the wonderful presentation. Now, let's move onto the last speaker of this webinar, Professor Jang Wook Choi at Seoul National University. Professor Choi received his Bachelor's from Seoul National University and PhD from Caltech under the supervision of Professor Jim Heath and also Professor Fraser Stoddart, who is the 2016 Nobel Laureate in Chemistry. Professor Choi performs many exciting researches in material science, especially as he will present today, binders for the lithium-ion battery. And he received numerous awards, including the Hong Jin-ki Award. And also, he received the Young Scientist Award from the President of Korea. And he was also selected as a highly cited researcher by the Clarivate Analytics. And today, the title of his talk will be “Connecting Battery Components: Advanced Binder Designs for Emerging Rechargeable Batteries.” Professor Choi, please.

최장욱:

Thank you, Professor Hyeon, for the nice introduction. As Professor Hyeon introduced, I'd like to talk about the binder, one of the essential components for the battery electrode. So, this could a bit different angle compared to our three speakers today who focused on the active materials. I think as we already discussed pretty much, we expect the battery market to grow markedly, particularly in the next 5 to 10 years. So, there seem to be also some coronavirus effects and Biden effects, which drive the overall technology more to be sustainable, which develop the battery technology even more drastically.

Beyond the materials, we need to worry about how we fabricate the battery electrodes. The typical procedure for the battery electrode fabrication is to mix three different components which are shown here, active material, polymeric binder, and conductive carbon in terms of a slurry, like the painting solution. And we adopt a certain recipe for the compositions among these three components. For example, 97 to 1.5 to 1.5 by weight. Once we have a slurry as shown here, then what we want to do next is just coat to the current collector. Then, we follow the coating, drying, and pressing of the electrode to complete the electrode. So, this is a picture for the coating process.

So, in order for this battery electric fabrication, we need a binder. So this is one representative binder for the lithium-ion battery cathode, which is called PVDF. And on the anode side, we usually adopt the aqueous processing so that we usually use a combination of CMC and SBR. By selecting this binder, in the end, we are worried about the following parameters. For example, adhesion, viscosity, chemical stability, electrochemical stability, and also cost of these polymer binders.

So, before getting into a more detailed story about the binder, since the binder is a polymer, we need to go from the very basic. Usually, a polymer is a repetition of a monomer. So, monomer, we determine the identity of the component, usually by functionality. Here is a series of functional groups being used for the polymer in many different cases. So once again, we determine identity and functionality. Then we just repeat this monomer. But that could be in a different manner. For example, we can just repeat the identical monomer, like continue only with an A, like a singular type, or only with a B. Or we can mix these two in a random manner to develop a random copolymer. Or we can combine, but into blocks. So, this kind of polymer is called a block copolymer. So, by choosing the polymer design, we are actually concerned about molecular weight of polymer or interaction with other particles or interchain interaction or intrachain interactions. So, once we determine the polymer structure, then we are going into a slurry solution. So here we have a schematic for the slurry solution, in which there are all the battery components. In this slurry conditions, now we are worrying about the polymer network, how polymer-to-polymer interacts with each other. That actually determines the very important rheological parameter, which is viscosity. So this viscosity and the other properties in the polymer level or in the more normal level actually determines the key properties for the electrode, like adhesion or resistance or stability.

Today, I'd like to introduce two representative cases where binders play an important role. The first example is the silicon anode. So, the three speakers already discussed about the high capacity electrode materials for both the anode and the cathode. Silicone is definitely a key high capacity material on the anode side. So, once we see this kind of specific capacity graph, compared to graphite on the left side here, silicone sits far beyond to deliver much higher capacity. So, this is definite an advantage, but there is a challenge, which is related to the volume change of the material.

We know the silicon undergoes a huge volume expansion when it is lithiated. So, once we have this volume expansion, there could be a series of failure modes. For example, the particle could pulverize. Pulverize means break apart. Or on the electrode level, the electrode also could delaminate toward the more unstable situation. Or we need to also be concerned about interface. So, there should be an SEI layer, but due to the huge volume expansion of silicon, this SEI layer could break apart and eventually much thicker, which actually is bad for kinetics and cycle life. So, in order to deal with this volume expansion problem, people have come up with various solutions. For example, nanostructures or binders. Of course, today I would like focus on binders.

Before going into more detail binder design, we need to first see what kind of a silicon material is actually being used for the industry. So, there are two kinds. One is a silicon-carbon blended one, the other is a silicon oxide. Usually X here is around one. So, these materials are being optimized to a very satisfactory level. But the thing we need to be worried about is there's no established binder design that works for the silicon content beyond the 10wt%. So, as we try to increase the energy density, we may have to increase the silicon content, but there's no particular champion binder that works for those cases.

So, for the binder design, we can usually see two different perspectives, so one is interaction with active materials. For that, we need to view the strengths of binding from the weak supramolecular to the strong supramolecular, to the fixed covalent crosslinking.

Also, whenever we design polymer, we need to consider polymer chain structures, so polymer structure. So, we can start from a very simple linear type to a more complicated three-dimensional structures like branched polymers or dendrimers. And these all should be taken into consideration when we design a binder for any particular battery electrode.

So, I'll show here some example of how we overcome the volume expansion problem of silicon anodes. Silicon particles could expand up to 300 percent when fully lithiated. 300 percent is actually quite a large number. But when we look at the polymer, on a single chain level, it expands at most a single-digit percent, and even in the network film, the expansion is as large as a double-digit percent. So, we better design the polymer to be more elastic to deal with all this scale mismatch. While all we are trying to develop high elasticity, one of my students actually found a very interesting world using the hydrogel, which is actually very elastic. So, as you see here, by stretching, there's a hydrogel, you were able to actually stretch even more than five times compared to the original dimension. And this stretchable hydrogel is actually very interesting because it contains some uncommon molecular structure, which is called polyrotaxane as part of this structure. So, there are a series of rings along the chain. There are two stoppers at both ends. So that ring can slide but never can get off of the chain. Very interesting phenomena from this highly elastic gel. So, even if you conjugate only 5 to 8 percent of polyrotaxane to a conventional acrylic polymer like PAA, you have drastically different mechanical properties. You have much higher elasticity compared to just a bare PAA.

Ok, once we have this level of high elasticity, then we might have some chance to deal with our micro-particle silicon. Micro-particle silicon is much more difficult to deal with because it usually breaks apart. Then, its electrode stability becomes much worse. But once we have some new structures containing polyrotaxane that I introduced in the previous line, then even in the case this micro-particle breaks apart, because of the high elasticity of the binder, they don't scatter. Rather, they coalesce together, having a stable particle structures as well as electrode structure. So, this is the animation how this polyrotaxane-based binder works. So, the rings slide here and there to just keep the particles stay together, but by de-lithiation now, the volume comes back and the binder position also returns to the original.

So, as Professor Hyeon briefly introduced, one of my PhD advisors received the Nobel Prize in 2016. He's the person in the middle here, Sir Frazier Stoddart. In fact, this kind of molecular family got recognized for the Nobel Prize. So, this molecular family is called a molecular machine. These molecular machines are based on mechanically interlocked cell structures. So, one example is called catanane. So, these two rings are interlocked with each other. Or rotaxane, a similar kind of polyrotaxane that I introduced as a binder has inter-sliding structures.

So, starting with the almost same thicknesses for these two binder cases, one as a conventional PAA binder, the other as rotaxane-based binder, after 10 cycles, the thicknesses actually became dramatically different. For PAA, the thickness increased from about 10 to 23. But for the rotaxane-based binder, thickness increased only to 12. So, the way the rotaxane-based binder controlled the thickness is particles just stay together. So even in the case they break apart, the high elasticity binder does not allow these particles to go away. They stay together, so controlling the overall thickness.

With this high elasticity of the binder, we were actually able to reach very high first Coulomb efficiency, which is very important for the cell design. So, we actually reached first Coulomb efficiency of more than 90 percent, which is very challenging for the silicon anodes. So the conventional binder shows only 81 percent.

For the cycle life, compared to PAA, which starts to degrade immediately from the beginning of the cycle, this rotaxane-based binder justice sustains for 150 cycles, confirming the stability of the electrode and the contribution of the binder.

Today, due to the time limitation, I just introduced one representative binder design, but I think that we can think about many different polymer variations. So, starting from the relatively early period, people introduced some cross-linked polymer systems or different types of natural polysaccharide polymers, or people have come up with ideas of self-healing to recover from any defect popping up during the cycling of a silicon anode, or 3D structures combined with charge to have a stronger interaction with silicon, and also recently we've reported metal coordination polymers to have a flexible but strong enough network in the electrode.

So, I'll move on to the next topic, in which the binder also plays a very important role, which is in the field of all-solid-state batteries. I mean, as the three speakers today discussed and also introduced in their talks, solid-state batteries are promising, with a big attention from the community. But I think beyond materials, I was concerned about how we actually scale up. In that sense, the binder is actually a very critical element.

As we already heard from other Professors, the main motivation of the all-solid-state battery is to replace the flammable liquid electrolyte with a solid electrolyte. By that, we can avoid fire hazard probably fundamentally. And also, now we have a chance to adopt some materials that could increase the energy density dramatically, like the lithium metal or the anodeless system. Or in terms of cell stacking, we can adopt the bipolar stacking, which could also increase energy density further. So, there are different classes of solid-state electrolytes. So, these three are the most representative: sulfide-based, oxide-based, and polymer-based. As Professor Whittingham introduced, PEO, polyethylene oxide, is the most representative polymer solid electrolyte. Each class has advantages and disadvantages, of course. The certified case that I like to focus on today has the advantage of high conductivity and mechanically soft nature. But it has chemical stability issues. So, you cannot just keep this one in the air. Then, for this sulfide-based all-solid-state battery, as I mentioned in the beginning, the key question that I like to address is how we actually scale up. We can think about two different approaches, like wet or dry. I think dry is at a relatively early stage, so we may need to wait for some time. For the wet process, the main difference compared to conventional lithium-ion battery is the need to include a solid electrolyte in the slurry or the electrode. For that, we need to find proper combinations for the solvent and binder, but we encounter a very serious challenge, which is related to polarity matching. So, solvent and binder are very difficult to match in terms of popularity.

There's a one report showing such a challenge from one Japanese group. They tested different solvents for the slurry with different donor numbers. So, from a low to high donor number. Once you hit a certain level, then you lose the ionic conductivity. Basically, you lose the crystal structure of a polar sulfide electrolyte. So that means we need to use a non-polar or less polar solvent for the slurry. But the problem is once we use are non-polar one, and then we lose adhesion, but once we use a polar solvent, then we lose chemical compatibility and dispersion, solubility. So, there is trade-off issues. Once you take one, then you lose the other. But we need both.

So, one way to avoid such dilemmatic issue is to design a binder in an unconventional manner. So, here's one approach based on so-called deprotection chemistry. What I mean by that is, in the slurries stage, we protect to match the polarity, but on the electrode fabrication level, particularly in the drying step, we deprotect so that we recover the adhesion of the electorate. This is the specific polymer design, so we protect the carboxylic acid group with t-BOC, which is shown here. So, during the deprotection step by heating, now we have a certain portion of the acid exposed as marked in the red box here. So, this acid functional group now functions as a adhesion site, so that electrode stability could be much more enhanced. And this kind of deprotection chemistry is actually well-developed and established in the field of organic chemistry or pharmaceutical chemistry. And actually, the level of synthesis is actually very low. Based on this new binder design, we were actually able to overcome the adhesion issue when we use a non-polar solvent. As a reference, we have this red sheet that corresponds to a lithium-ion battery electrode adhesion, which is around 10. One of the common binders that people use for the sulfide-based all-solid-state battery, BR, butadiene rubber, showed a much lower value. But once we adopted this deprotection binder, we reached much higher like 20 and even above.

Using this new binder design, we were able to extend the cycle life quite dramatically compared to the BR case here for the 50 cycles. If you look at the cross sections, the way this new binder extends cycle life becomes more straightforward. For example, compared to the butadiene rubber electrode, in which we see many cracks in the particles or between the particles, the deprotect binder shows much fewer cracks and voids. So, out of this, we can tell the new binder design improved particle mechanical stability as well as the interfacial stabilities.

So even the general public is interested in this new technology, all-solid-state batteries. If you look at what's happening in the industry at the moment, many of the global car OEMs like Volkswagen, Hyundai, Ford, invest quite a bit on some new startup companies. So, these startup companies are developing technology based on the different solid electrolyte materials. Of course, the field is still at the early stages. There are some controversial reports about their success and promise or feasibility. But the key message here is that no matter what material they pursue, as long as they adopt a solution-based process as we do for the current lithium-ion batteries, we need to develop the functional and scalable binders for cost-effectiveness and scalability.

Just to summarize, binder may not be a passive component anymore, so there must be advanced polymer design implemented into an electrode. The electrodes or cells that require new binders actually are a good number. So, for example, silicon anode that I introduced as a first part, lithium metals also need to have a better binder, all-solid-state batteries I introduced in the second part, high nickel and sulfur cathodes, which are all receiving good attention, need better binders. Basically, we are facing new challenges from these new electrodes and cells, but we should be able to find better solutions and also we need to be worried about how we go from the lab to the manufacturing site. For that, of course, we need to care about key aspects of polymer like functionality, viscosity, and interaction with other components of the electrode.

With that, I'd like to thank all of my students who particularly participate in the projects that I introduced today, and also the collaboration sites and the funding agency. Thank you so much for your attention. Thank you.

현택환:

Thank you very much, Professor Choi, for the wonderful presentation. Now we have listened to four wonderful presentations and discussions by four eminent speakers in the battery research area. And I also have to thank all of you for connecting to YouTube to listen to this webinar from the beginning to this time. I really appreciate that. Thank you very much, all. Thank you.