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Undergraduate

JEFFREY LONG:

CARBON CAPTURE AND SUSTAINABILITY

Jennifer Cherone, Kapil Gururangan, Jared Rosen, Prashant Bhatt, Elaine Owen, Manisha Rai

Professor Jeffrey Long graduated with his doctorate from Harvard University in 1995 and entered UC Berkeley as a National Science Foundation Postdoctoral Fellow from 1996 to 1997. Since then, he has researched metal organic frameworks to push environmental technology forward. With a mind towards creating sustainable energy and cleaning current fuel sources, he has toyed with the mechanism of carbon-capture technology that could purify the emissions of smokestacks and reduce carbon dioxide emissions. With the eminence of climate change, Professor Long's research is both topical and immediately relevant to the sustainable energy movement.

WE WERE MAINLY LOOKING AT TWO OF YOUR PROJECTS, THE FIRST ONE BEING THE DISCOVERY OF MOLYBDENUM-OXO COMPLEX AND THEN YOUR WORK USING METAL ORGANIC FRAMEWORKS IN CARBON CAPTURE TECHNOLOGY. HOW DID YOU FIRST GET INVOLVED IN RESEARCH REGARDING SUSTAINABLE ENERGY?

"You never know where you're going to head when you're a synthetic chemist; something really new could take you in any direction."

Long: That's a good question – it sort of happened by accident. We are generally interested in making new inorganic materials, so that means figuring out how to make connections between atoms other than carbon-based atoms that organic chemists work on. In our research, we found a basic method for making these solids that had a porous structure, so they would have holes in a three-dimensional network of atoms. Solids like that turn out to be useful for absorbing gases into the pores, so they're kind of like a sponge to soak up gases like carbon diox-



Figure 1. Long standing in front of a working bench.

ide, and so on. We had a synthetic technique for making those kinds of solids and when you make something new in the lab, you're always interested with: what can do with it, what are its properties, what's special about it that we can take advantage of that nobody's ever done before. So we started thinking about that, and at that time, around 2002 or 2003, the Department of Energy had a big push for research on hydrogen storage materials and those were intended for use in cars that are fueled by hydrogen instead of gasoline. People are interested in that because if you burn carbon in gasoline, then you produce carbon dioxide, which is bad for life on earth, but if you burn hydrogen or use a hydrogen fuel cell to power your car, then the by-product is water. It's a very clean technology for driving around and so we thought our approach to making materials might be applicable to storing hydrogen at high capacity in cars. It's important for hydrogen cars because now, hydrogen is such a volatile molecule that cars struggle to travel long distances before you have to refill them. We started working on targeting our new materials towards that application. We've worked for almost ten years on making new hydrogen storage materials that might one day be used in hydrogen cars in the fuel tank. More recently, we've been thinking about other applications and got interested in carbon dioxide capture. So you never know where you're going to head when you're a synthetic chemist – something really new could take you in any direction.

SO IN REGARDS TO THE CARBON CAPTURE STORAGE PROJECT, WE SAW THAT YOU RECEIVED A LOT OF FUNDING FOR IT LAST YEAR. WHAT'S YOUR CURRENT STATUS ON IT?

Long: We have a big center here at Berkeley, which is the main center supported by the Department of Energy for basic research on gas separations – particularly on capturing carbon dioxide. This is a big program that involves probably fifty or sixty researchers total and my lab is involved in part of that effort. We have probably ten to twelve researchers in my lab who are contributing towards that effort. The focus there is to make new materials that will reduce emissions from power plants, particularly carbon dioxide emitted from power plants. I don't know how much you know about this, but right now, CO₂ levels in our atmosphere are at 390 parts per million and that's higher than we've had in the last 400,000 years. So there's CO₂ in the atmosphere at this really high level and it's going up very rapidly and it's thought to be tied to man-made generation of carbon dioxide by burning fossil fuels. You can actually see that because if you look at the oxygen concentration in the atmosphere, the rise in CO₂ concentration is perfectly mirrored in the drop of oxygen concentration. So for every molecule of fossil fuel that you burn, you create carbon dioxide and also use up oxygen – you use the oxygen O₂ atoms in air to make the carbon dioxide. You can see that corresponding drop so it is being generated by burning fossil fuels. We'd like to do something about this because there is a good correlation between carbon dioxide in the atmosphere and the temperature of the planet – that's something that physical chemists have known for a hundred years. The need is to stop emitting CO₂ and a lot of research is pushing to get renewable energy sources that could replace burning fossil fuels – solar energy, wind energy, waves, geothermal, nuclear energy. All these things could replace burning fossil fuels. Our research on the molybdenum-oxo catalyst was about trying to use solar energy to make hydrogen from water and use hydrogen as a fuel. The carbon capture project is about directly addressing the immediate problem of CO₂ being emitted from power plants. Worldwide, we're making about 30 billion tons of CO₂ per year from burning fossil fuels – that's a staggering amount that most people can't get their mind around. Half of that CO₂ is coming from those power plants for electricity production and heating your homes. About a third of that CO₂ emitted is coming from transportation and most of that are passenger vehicles burning gasoline in your car. Those are two of the biggest problems that we have. So to reduce CO₂ emissions from power plants, we've got a number of strategies. One is to use some material that can make the carbon dioxide in the gas stream emitted from the smokestack of a power plant stick



Figure 2. Data being examined by researchers in Long's laboratory.

to that material. Then we can remove all the CO₂ from that emission stream and it's a huge amount of CO₂, so we have to think what we're going to do with it all. You might think that we could make polymers or something useful we could make out of carbon dioxide, but it turns out that this is so much carbon dioxide that there's no market for all of it. There's nothing you could make that there could be a market for. One possible exception is if you could make a fuel at low-energy costs – a fuel like methanol – from CO₂, then we could use that in portable applications and transportation. That still wouldn't use all of it. So the main plan right now is that we would like to remove the CO₂ from this flue gas and then store the carbon dioxide underground. Ok, and so storing carbon dioxide under ground is something that is already being implemented. One way to get oil out of the ground is to force it out with compressed carbon dioxide and so when this is done they recover the oil from some geologic formation and the carbon dioxide that you used to push it out is actually maintained in that [geologic] formation. So there are large geologic formations where you could inject carbon dioxide, displace oil or salt water (you know there are large salt water aquifers). And so there is a current plan to implement technology that would take carbon dioxide out of the flu admissions of a power plant, compress it and store it underground in these geologic formations. And when you do that you need to make very sure that you have good geologist so that you put carbon dioxide underground and it doesn't come back up, right. If it comes back up then you have wasted a lot of effort. So our research is actually about trying to make new materials that can grab the carbon dioxide out of the flu gas with minimal energy cost for being reused. Right, because when you bind the CO₂ and then have to regenerate your absorbent to remove the CO₂ to put it underground there is an energy penalty, you have to heat up the material. And so we are trying to design materials that can do that very efficiently



Figure 3. A typical fume hood used in the laboratory.

without using a lot of the power that is being generated in the power plant.

ARE THEY CURRENTLY USING SOME FORM OF CARBON CAPTURING MATERIAL? WE READ ABOUT DIFFERENT STATISTICS ON THE AMOUNT OF ENERGY DIFFERENT MATERIALS TAKE. ARE THOSE CURRENTLY BEING USED?

Long: They are currently being used, but not on so massive a scale. We have so many power plants around the world and you know almost none of them are currently using CO₂ capture technology and the reason for that is just a business reason. There is no market for this CO₂ that they would capture really. And so if you implement this technology it costs you extra money to attach to your power plant this apparatus to remove the CO₂ and until governments regulate carbon dioxide emissions and try to prevent this buildup, which is really effecting out planet in a very serious way companies aren't going to do it because they just lose money by doing it. But it is expected that scientist will eventually get politicians to listen to them and implement these kinds of regulations. And as soon as that comes into place, then all of these companies will be looking for technology that they can use to stop emitting the CO₂. So there are a lot of large-scale projects that are trying to develop technologies to be used when that happens.

WHAT MAKES THE MOLECULES YOU ARE DESIGNING MORE EFFICIENT THAN THE MOLECULES ALREADY BEING USED. WHAT ARE YOU SEEKING TO IMPROVE THE EFFICIENCY OF?

Long: The best current technology for doing this is to take molecules that have an amine group, which is a really strong base. So molecules like monoethanolamine are these little organic molecules with an NH₂ group on the end. The NH₂ group is important

because it reacts with CO₂ to make a nitrogen carbon bond. That's how it selectively grabs CO₂ from the Scatstreme. In order to do that, they have to put that molecule in water, into a solution of water. So the removal of CO₂ is based on these solutions of amines in water. When you regenerate, when you want to get the CO₂ captured back out, and reuse your solution and have to use a huge amount of heat because the heat capacity of this aqueous solution is extremely high. Its thought that solid absorbance with a very high surface area could have a much lower heat capacity for doing the same thing. We should be able to get the energy penalty from around 30% of the energy being produced, or electricity being produced by a power plant, down to about ten percent. That's a huge energy savings. That's our target, to make that difference and come up with what would be the next generation of what would be more efficient materials for capturing CO₂.

YOU TALKED ABOUT STORAGE, HOW YOU WOULD STORE THEM UNDERGROUND. ONE THING WE WERE WONDERING WAS WOULD THE CAPTURED MOLECULES STAY UNDERGROUND? WOULD THERE BE ANY FEASIBLE RISKS?

Long: The important thing is that whatever we're using to capture the CO₂, we have to reuse it because there is so much CO₂ that you can't produce this much material and then not reuse it. You need to be able to reuse it hopefully 1,000 and millions of times. The CO₂ stored underground would be pure CO₂. The biggest concern is that you might put it into a place where it isn't stored for a long time. The objective is to put it underground so it doesn't come up for hopefully the next 1,000 years. In the mean time, we can find other renewable resources besides burning fossil fuels. The cycle life of this CO₂ in our atmosphere is about 200 years so eventually CO₂ will start to come back down. That is one of the pressing concerns. There are other possibilities; you might have an earthquake so you have to be careful about where you put this carbon dioxide. There is quite a bit of research on carbon storage. The Department of Energy's main research facility for carbon storage is also at Berkeley. There is a separate center for figuring out the best ways for storing CO₂ underground. That is at Lawrence Berkeley Lab here. We work on the capture side, so I know more about that than the storage, but both of those programs are here at Berkeley.

GOING BACK TO WHEN YOU SAID USING A SOLID TO CAPTURE CARBON DIOXIDE WOULD BE MORE EFFICIENT THAN USING THE WATER, IS THAT CURRENTLY BEING USED WIDESPREAD TODAY?

Long: No.

IS THAT GOING TO BE SOMETHING THAT IS USED IN THE FUTURE?

Long: These are brand new materials that nobody has seen or tested before. Before you would start implementing them in this application, you have to really test all kinds of things to see if they're viable. We are at the initial stages of creating these materials that have a very good preference for binding carbon dioxide over the other gasses in this gas mixture, which is mainly nitrogen. You also have to make sure that you can recycle them again and again. That they are stable to heating and cooling as you regenerate the material time and time again. Also, that they are stable to all the impurities that come along in flue gas. Flue gas has some water in it, a little bit of oxygen, some molecules of SO₂, and NO₂ in tiny amounts. You want to make sure that the material can also tolerate exposure to that time and time again with out decomposing. We are really at a basic research stage in discovering materials and testing them in terms of their properties, how they interact with other gasses. If we find very good candidates, the next step would be to do a larger scale test. There are a lot of things that happen before something would be ready to be implemented.

IN THE FUTURE, COULD YOU SEE THIS TECHNOLOGY WITH CARBON CAPTURE BEING ADAPTED FOR SMALLER USES, FOR EXAMPLE IN CARS?

Long: It's possible. You could imagine you know okay we're burning gasoline, CO₂ is coming out of our tailpipe, and we could put a little unit on our car, and capture the CO₂. It's a lot more difficult for these applications where you're mobile. Your car has to get you down the road and if you start adding weight to the car, then it cuts down on the efficiency of using the fuel. And so it's actually a much harder thing to do these mobile capture applications versus a stationary application where you don't have to worry so much about adding weight if you're just a power plant on the ground. So it's possible, but it's harder to implement than with the power plants. That would be another target but we're going to start with easiest place where we can make a big difference and that's these power plants where there's a huge amount of CO₂ being emitted in a very concentrated source.

SWITCHING TO THE OTHER PROJECT NOW, THE NEW WATER-SPLITTING CATALYSTS THAT YOU'RE WORKING ON, I THINK WE'RE ALL WONDERING IF YOU COULD EXPLAIN HOW THIS PROJECT GOT STARTED INITIALLY?

Long: Yeah this was also somewhat serendipitous,



Figure 3. One of two Micromeritics ASAP200 Gas Sorption Analyzer used in the laboratory.

you know we were working on magnetic molecules so we have had, since the lab started, a project where we try to make molecules that behave like tiny little bar magnets and in the course of that research, one of the students made a molecule that turned out to react with water to generate hydrogen. I actually realized that that might be possible because I had been talking with one of my colleagues here in the department, Chris Chang, who had a research program on trying to make catalysts for water splitting (for making hydrogen from water). And so we'd been talking about it a lot and we'd been talking about the fact that molybdenum could actually do this reaction in another molecule that was studied by somebody else but that other molecule had a lot of problems with it. And so when the student in my lab made this molecule I realized it could in many ways be quite similar in reactivity to this other known molecule. And so we suggested to the student, "okay let's try this, let's see what happens," and sure enough, it does the reaction where you start with a molybdenum center that has a very weakly bound molecule, and water can come in and displace that molecule, and then hydrogen is actually released from the water molecule to the gas phase, and you form this molybdenum-oxo unit. That's just a one-to-one reaction between one molecule of water and one molecule of this molybdenum-centered molecule. In order to make something useful, you need to be able to recreate the species that did the initial reaction with water and so that means you want to be able to use that molybdenum in a catalytic cycle, where it's feeding back and reacting with a new molecule of water to generate more hydrogen. And so, in order to get this molybdenum-oxo compound that we've made in the initial reaction with water to come back and react with a new molecule of water, we had to feed it electrons and protons. And so the electrons, initially, in testing out this idea, come from an electrode (we created an electric current from an electrode and the electrons flow from



Figure 4. Two of several high-temperature furnaces for solid-state reactions.

the electrode surface into our molecules and then we need to bring in new water molecules that can react and hydrogen will come off and so a single molybdenum center on an electrode surface can do this reaction again and again and generate lots of hydrogen without failing. And so that's very important but if you can get that to work then you might ultimately be able to also do it being electrons that are generated using sunlight. The idea ultimately for these catalysts is to couple them with solar photovoltaic technology where the sunlight is used to excite an electron, which can then be fed to the catalyst to generate the hydrogen. Ultimately if you can make these catalysts so they're very efficient then you could have a good conversion of sunlight into hydrogen with water supplying the protons.

IS THAT SOMETHING THAT, GETTING BACK TO THESE MOBILE APPLICATIONS, YOU COULD SEE BEING APPLIED TO CARS? SO YOU PARK YOUR CAR IN THE MIDDLE OF THE SUMMER AND YOU'VE GOT A TANK OF WATER INSTEAD OF GAS, COULD YOU—

Long: You could do it that way. You can buy electrolyzer units that can electrolyze water and create hydrogen and then you can use that to power your car. The problem with that [mobile application] is providing the electrons to do the reaction requires a really serious battery. Batteries are very heavy, bulky technology right now, so until those are really improved dramatically, that's going to be a hard way to do it. And you could use solar panels on your car but then if the sun's not shining or you want to drive at night then you've got a problem. But there are companies that are seriously developing solar cars that would basically do what you're suggesting, that could take the electricity and power your car directly if the sun's shining, or if not, use it to make fuel (like hydrogen) to store, but the batteries are not there for that technology yet. A lot of people think that instead of batteries, for mobile applications, it's more likely we'll

store the energy as hydrogen. Even though it's difficult, you can get to higher energy densities that way than with batteries.

SO, YOU SAID IT DOES STILL TAKE A LOT OF ELECTRICITY TO REGENERATE THE CATALYST, THOUGH, BUT IT'S STILL BETTER THAN IF YOU DIDN'T HAVE THE CATALYST.

Long: Yes, right so essentially you can take an electrode and if you turn up the voltage high enough, you've probably seen this in freshman chemistry, you can make hydrogen at the electrode's surface. The catalyst just lowers the voltage required to make the hydrogen from the water. And so instead of having to apply a large amount of energy, you can use the catalyst to apply less energy. Splitting water can be done electro-chemically, or with really intense heat (thousand plus degrees), nuclear energy, but sunlight is so abundant, so it would be a great source for that energy, which is why so many people are working on that.

IN ONE OF YOUR PAPERS YOU ALSO MENTIONED HOW ORGANIC ACIDS AND SOLVENTS ARE USED FOR SALT COMPLEXES THAT GENERATE HYDROGEN FROM SPLITTING WATER BUT THAT THIS NEW MOLYBDENUM COMPLEX WOULD BE ABLE TO RUN ON NEUTRAL PH?

Long: Yeah, so there are some molecular catalysts that have been found by other labs where they could take protons and make hydrogen on an electrode surface but they wouldn't be effective in water because they would decompose in water. So there are two problems with that: One is, if you have to use some acid that you're making in an industrial process as a source of hydrogen, that's very expensive and probably not sustainable. Second, there's also this organic waste that comes about if you use some organic acid for example. And so if we can use water as the acid, (water can be acidic, the protons can come off), that's the most abundant, most sustainable source of protons that we have. And it's really good because ultimately when you use the hydrogen you recreate water, so it's a nice cycle, where you're getting hydrogen out of water, and then regenerating the water when you use the hydrogen as a fuel.

AS FAR AS THE PRIMARY DIFFERENCE BETWEEN THIS CATALYST [AND OTHERS], WE READ ABOUT HOW THERE'S OTHER CATALYSTS THAT CAN DO THE SAME THING LIKE PALLADIUM, BUT IS THE MAJOR DIFFERENCE BETWEEN THEM JUST THE PRICE DIFFERENCE?

Long: Yeah, so right the now, the best catalyst for



Figure 5. TA Instruments Differential Scanning Calorimeter DSC Q500.

doing this reaction is probably platinum, but platinum is not very abundant and extremely expensive. And so there's no way we can use this on the massive scale that's needed. There's just not enough platinum, and if even if you started trying to build a lot of these devices, the price of platinum would skyrocket even further (right now it's extremely expensive). We just don't have enough platinum to do that. So cost is a real consideration, not just cost but abundance of whatever you're using for these applications. You have to be able to find enough of this material without doing serious damage to the planet to be able to make it a big, widespread application.

SO WHERE DOES THIS MOLYBDENUM METAL ORIGINATE FROM?

Long: It occurs in minerals, in a lot of places. It's actually one of the more abundant metals. There are many more abundant metals, but it's actually one of the most abundant metals in the ocean, after iron and copper. So there's quite a lot of it in seawater compared to other metals. As a result of it being abundant in a lot of places and easily extracted from those resources, molybdenum is relatively cheap compared to platinum.

IS THERE ANY REASON TO WORRY THAT THE MOLYBDENUM WOULD BE SLIGHTLY HARMFUL OR TOXIC?

Long: Molybdenum is a metal that's also found pretty commonly in nature, probably because it's in the oceans, so there's always a concern about toxicity. For a catalyst, you're generally using small amounts of the material, and there's no reason to think that this would be particularly harmful to the environment or to humans. But it is something, before you started giving these out to everybody, you'd want to

test whether there's a toxicity issue. So for a new molecule that nobody has ever made before, it's pretty much unknown, and so you'd want to do those kinds of tests. That's not something we do, that would be down the road.

SO I THINK WE ALL KIND OF REALIZE THAT YOU'RE STILL IN THE EARLY STAGES OF TESTING THIS MOLECULE, BUT HOW FAR/ HOW LONG AWAY MIGHT COMMERCIAL APPLICATIONS BE?

Long: That's really hard to say. I get a lot of phone calls and email messages from companies and business people just asking that same question, "How close are you and can we help you bring this to commercialization, how ready is the technology," and this is technology that has now been licensed by a company called Phoenix International, and they're interested in doing sort of the next step of testing and evaluation to see if it could be used on a big scale. That's more in the domain of industrial research and chemical engineering, and it's not the kind of basic science that we're good at. But for something like this, it'll take at least 5, more normally 10 years before there's actual products. With solar energy there's such a driving force and need, though, that things can be accelerated if they really make sense. There are things about the catalyst that we really are trying to improve with our research. Right now, for example, the potential that you have to apply to generate the hydrogen is still higher than we think we could get to. So we're working on finding new variations of the molecule that could work at lower applied potentials (less energy input). And so the further we can reduce that, the more and more excited people are going to be about putting money in to develop it further.

I DON'T KNOW IF YOU'RE ALLOWED TO ELABORATE ON WHAT THESE VARIATIONS MIGHT BE?

Long: Well, it's probably not interesting that for me to give you the details, but for example, this catalyst has a molybdenum center and an oxygen atom bound to it, but also has a surrounding organic molecule that's the ligand that stabilizes the molybdenum center in solution. What we can do is we can make subtle changes to the organic part of this molecule that change the electronic structure at the molybdenum and can affect that potential required for making the hydrogen. We're trying modifications on that organic part that we think will drop the energy required to do the reaction. We do that using both this vast background of chemistry that many chemists have done and our chemical intuition, but also using theory and computational methods. We have a collaborator, Martin Head-Gordon on the faculty here

who's a graduate student who is doing computer calculations to try and predict changes to the molecule that would drop the potential required to make hydrogen. All of these energy problems are large and complex things; a place like Berkeley has a huge advantage for working on those problems because we have experts in all these different areas that can work together. They are such large, complicated problems that it's hard for any one scientist to get all of the different areas of expertise needed into their head. This is really a great place because it has this huge concentration, not just the university has a big department for lots of sciences with lots of people, but Lawrence lab has a huge number of scientists and large-scale instrumentation that other places don't have. And so that's why there's such a huge concentration of science here, science and engineering.

AND ON TOP OF THAT, BERKELEY IS THE PLACE FOR SUSTAINABLE ENERGY.

Long: Yeah. Definitely, the public surrounding us are very favorable toward that idea, which is good, and the state of California is also very favorable for that, we are way ahead of the rest of the country. But this concentration of science and collaboration between makes it possible to do that energy research, which has a lot of complicated issues feeding into it. Yeah, so this is a great place for us to be.

IS THE ULTIMATE GOAL TO PRETTY MUCH REACH THE POTENTIAL OF PLATINUM?

Long: That would be great. That is possible, we know that's possible because actually nature has enzymes that do this reaction, that make hydrogen from protons that are fed in and electrons that are being fed into the reaction center. These hydrogenase enzymes can operate at very, very low voltages. They can do this reaction at near the thermodynamic minimum, and so they can actually beat platinum. Those are discrete molecular units that can do this reaction at little energy cost. Our hope is to be able to get to that level of competence. That sounds like, "why don't we just use these biomolecules to do it?" and some people are trying that, but one disadvantage is that the biomolecules are really large molecules, and so if you're thinking about the solar flux and the number of photons hitting a semiconductor to hit electrons, in order to keep up with the solar generation of electrons, you actually need to be able to have a high density of catalytic sites per surface area. If your biomolecules are large, then it's hard to accomplish that. We're actually hoping to beat nature in terms of size of the molecules that can act as catalysts. It's hard to beat nature, but if you think about it, we created airplanes that can fly faster



Figure 5. Quantum Design MPMS2 SQUID Magnetometer.

than birds, and they are a completely different construct, without feathers or flapping. The same can be true for chemical reactions, right? The way that nature does it has a reason and it's evolved to be very efficient, but in an industrial process the conditions are completely different than what happens in nature. You can actually do things sometimes much more effectively by quite a different type of system.

IMAGE SOURCES

<http://alchemy.cchem.berkeley.edu/tour.html>
Portrait provided by Dr. Long.