C2CNT: Cost incentivized greenhouse gas mitigation to end global warming

C2CNT (CO_2 to Carbon Nanotubes) is a comprehensive solution to climate change, a principal challenge facing the planet today. We've discovered the inexpensive transformation of the greenhouse carbon dioxide into a widely useful and highly valued product. In our C2CNT process, CO_2 is directly transformed to carbon nanotubes (CNTs) with remarkable properties of lightweight strength greater than steel, flexibility and high conductivity. C2CNT provides the most compact form to capture CO_2 and mitigate climate change. The C2CNT market provides lightweight cheap replacements to metals, new bullet and "taser" proof textiles, stronger cement composite building materials, and expanding applications in industrial catalysis, batteries and nanoelectronics.

C2CNT is a low energy, high efficiency process in molten carbonate electrolytes, and provides a reaction pathway to transform the greenhouse gas into a high value commodity. CO_2 is bubbled into the carbonate, dissolves to form more carbonate, then electrolyzed, evolving oxygen at the anode, and producing carbon nanotubes grown at the cathode. The carbonate electrolyte is not consumed, the process does not require rare or noble materials, and the net reaction is CO_2 splitting into carbon nanotubes and O_2, for example using Li_2CO_3 as the electrolyte the chemical process is:

Dissolution: $CO_2(gas) + Li_2O(soluble) \rightarrow Li_2CO_3(molten)$

Electrolysis: $Li_2CO_3(molten) \rightarrow C(CNT) + Li_2O(soluble) + O_2(gas)$

Net: $CO_2(gas) \rightarrow C(CNT) + O_2(gas)$

Climate Change is a principal challenge facing the planet today. During the industrial age massive quantities of greenhouse gases, principally carbon dioxide, have been released into our atmosphere through the combustion of our fossils to meet humankind's industrial, transportation and energy needs. These greenhouse gases trap infrared heat increasing the temperature of the planet (global warming) at an accelerating rate and causing species extinction. The C2CNT process developed by the Licht group has already progressed to the semifinal phase of the Carbon XPrize competition. The Carbon XPrize is a global competition to generate the most valuable product from carbon dioxide, from the organization that helped the spawned the commercial space industry through a similar XPrize competition (described at: http://carbon.xprize.org/).

Popular & Technical Media C2CNTdescriptions

*Licht interview on BBC World Newshour; click on the audio button at "The Bottom of the Barrel?" This will start the Newshour, and slide ahead to the interview between time 18:52 and 23:00.14.
http://www.bbc.co.uk/programmes/p02yxbv0

*Licht press conference at American Chemical Society National Meeting
https://www.youtube.com/watch?v=kQBlpENiFzo

*Licht C2CNT interview on public television (scitech)now episode 218 at:
The introduction, interview & our CO_2 capture animation runs from 00:00-00:34 and 13:44-19:22
http://www.scitechnow.org/videos/episode-218/Year three milestone: Global deployment, starting a C2CNT 10 yr plan to lower atmospheric CO_2 to < 400 ppm.

Google "Diamonds from the sky Licht", or "Licht Cement Power plants"
Descriptions in *Science, Forbes, MIT Technology Review and other popular reports follow…*

nano werk

Posted: Mar 21, 2017

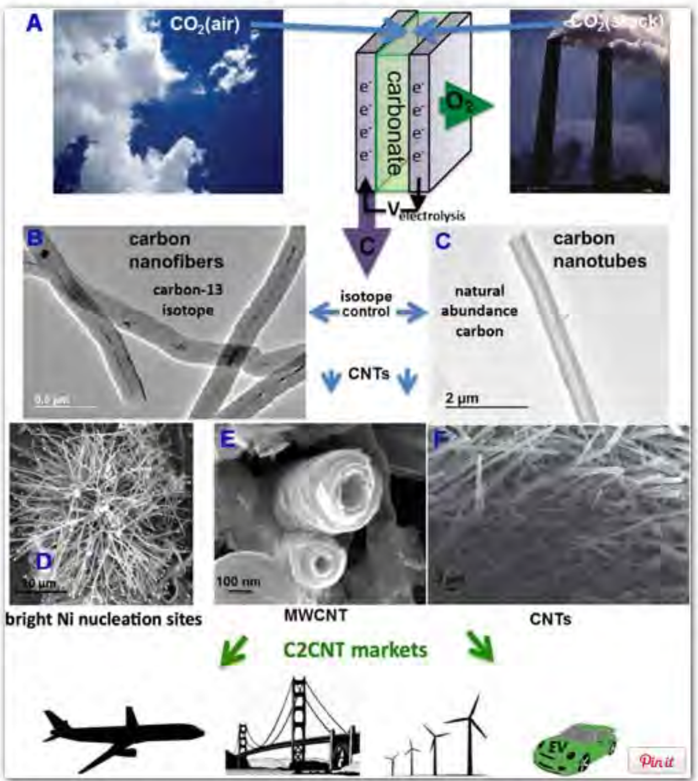
www.nanowerk.com/spotlight/spotid=46170.php

Transforming greenhouse gas CO2 into carbon nanotubes

(*Nanowerk Spotlight*) The cement industry is one of the largest sources worldwide of carbon emissions, accounting for around five per cent of global emissions. Two thirds of these CO_2 emissions are released during the chemical process of burning limestone for cement production and can only be cut by extracting the CO_2 from the emissions in one form or another.

In a previous *Nanowerk Spotlight* we looked at how nanoengineering of cement-based materials can result in outstanding or smart properties ("Nanotechnology in the cement industry – a patent analysis").

Now, in two new studies, researchers show that cement plants can have their carbon dioxide exhaust eliminated while co-producing carbon nanotubes.



Scheme for the electrolytic synthesis of carbon nanostructures from carbon dioxide: (a) the source of CO_2 can be either smoke stack concentrations of CO_2 or air (without requiring pre-concentration) dissolved in molten carbonate, (b) and (c) isotope controls formation of carbon nanotubes or nanofibers, the more valued CNTs are made from the less expensive natural abundance CO_2. High oxide concentration produce tangled morphologies (d) while low oxide produces straight nanotubes (f). (e) Bright nickel nucleation sites, as identified by EDS, initiate CNT growth. Lower panel: The CNTs and carbon nanofibers provide high conductivity and superior carbon composite lightweight structural materials for jets, bridges, wind turbines, and electric vehicle bodies and batteries. (© Elsevier) (click on image to enlarge)

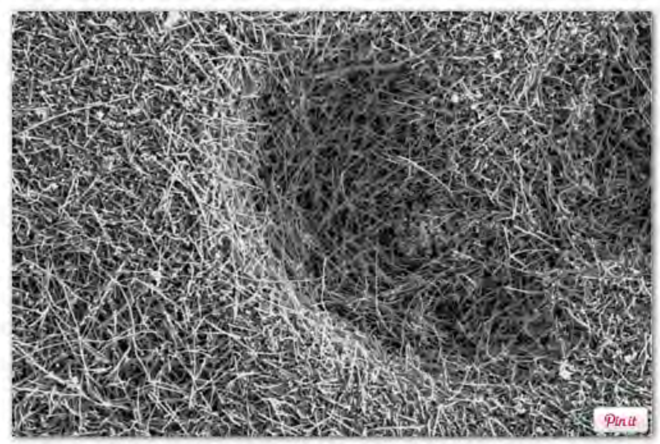
"We have demonstrated that with our C2CNT (carbon dioxide into carbon nanotubes) process, a wide portfolio of tailored carbon nanotubes (CNTs), such as those with special shapes or conductivity can be made," Stuart Licht, a professor of chemistry at George Washington University, tells Nanowerk.

In the first paper, in *Journal of CO_2 Utilization* ("Transformation of the greenhouse gas CO_2 by molten electrolysis into a wide controlled selection of carbon nanotubes"), Licht and his team present the transformation of CO_2 into specific, controlled carbon nanotubes.

This study presents a straightforward process that transforms CO_2 to carbon nanotubes by molten electrolysis with inexpensive (nickel and steel) electrodes and low voltage. This synthesis consumes only CO_2 and electricity, and is constrained only by the cost of electricity.

"Control of electrolysis parameters opens up a wide portfolio of CNT morphologies including hollow or solid, thick or thin walled," says Licht. "Our portfolio also includes doped CNT. Molten carbonate electrosynthesized boron doped CNTs have high electrical conductivity. The CNT from CO_2 synthesis remains single step (one pot) in which a specific impurity is dissolved in the electrolyte to achieve a desired doped CNT characteristic."

The C2CNT technology is applicable to the direct removal of atmospheric CO_2 or the elimination of industrial CO_2 from smokestacks.



SEM image of carbon nanotubes produced from CO_2 at the cathode during constant current electrolysis in a molten Li_2CO_3 electrolyte. (Image: Licht Group, University of Washington) (click on image to enlarge)

In the second paper, also in the *Journal of CO_2 Utilization* ("Co-production of cement and carbon nanotubes with a carbon negative footprint"), Licht presents the use of C2CNT to retrofit cement plants.

Cement production today has a massive carbon footprint and simultaneously releases CO_2 both from limestone and from fossil fuels, and hence cement plant smokestacks have much higher CO_2 content (5 times higher than gas fired electric power plants).

This study compares conventional cement plants to alternative C2CNT cement plants and shows:

In the C2CNT cement plant CNTs are produced by molten carbonate electrolysis of CO_2.

The conventional cement plant emits 1.1 ton of CO_2 per ton cement produced.

The C2CNT cement plant emits no CO_2, converting it to a valuable CNT co-product.

Per ton CO_2 avoided, the C2CNT cement plant consumes $50 electricity, emits no CO_2, and produces $100 worth of cement and ~$60,000 worth of CNTs.

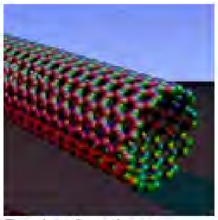
Scaling up the C2CNT process to work with commercial plants is the ongoing second stage of the researchers' investigations. As part of this effort they have advanced to the semifinals of the Carbon XPrize as the C2CNT team. The Carbon XPrize is a global competition for research teams to transform CO_2 from a power plant into the most valuable product.

IChemE

The Chemical Engineer

Monday 04 July 2016 - The Chemical Engineer... news and jobs from the chemical, biochemical and process engineering sectors

News - full story



For 1 t of methane burned, a plant using the process would make US$835 worth of electricity and around US$225,000 of nanotubes

22/06/2016

Turning captured carbon into nanotubes

1 t of gas would make US$225,000 worth of nanotubes

Helen Tunnicliffe

POWER stations could one day capture CO_2 and convert it directly into sought-after carbon nanotubes and nanofibres, after engineers in the US proved that their method is thermodynamically feasible and financially favourable.

Capturing CO_2 from fossil fuel-fired power plant emissions is increasingly seen as a vital technology to reduce the world's greenhouse gas emissions, but finding suitable storage sites for the captured gas can be a problem. Converting the gas into useful products, such as sodium bicarbonate, or carbon nanotubes (CNTs), which are used in batteries, consumer electronics, aeroplanes, and athletic equipment, would be a better alternative, but such processes can be costly, both economically and thermodynamically. Stuart Licht and his team at George Washington University, have found that their process to produce carbon nanotubes and nanofibres (CNFs) from the captured emissions of a combined cycle power station is feasible on both counts.

Last year, Licht and his team developed the process to convert CO_2 into carbon nanofibres. They estimated at the time that 1 t of the nanofibres would cost around US$1,000 to produce, far less than the value of the finished product. They have since discovered that adding a small amount of nickel catalyst to the process instead produces hollow carbon nanotubes.

The process uses a molten lithium carbonate (Li_2CO_3) electrolyser, at temperatures of around 750°C. The hot captured CO_2 dissolves into this. Using electrolysis, with a current generated by electrodes, the CO_2 splits to form oxygen gas and pure carbon. The carbon forms into nanotubes in the presence of the nickel and zinc catalyst. Oxygen generated in the process is fed back into the combined cycle power station, so although some electricity is needed for the electrolysis process, the oxygen has the benefit of boosting its electricity-production efficiency. Energy is saved in various other ways throughout the process, including by using hot CO_2 directly from the turbines, which more easily reacts and has significant enthalpy savings compared to capturing cool CO_2 in a conventional CCS plant.

Licht and the team say that per ton of methane burned, a conventional combined-cycle power station with no CNF facility produces 9,090 kWh of electricity, which at current rates in the US equates to US$909, and emits 2.74 t CO_2, while a so-called CC CNF (combined-cycle carbon nanofibre) plant would produce 8,350 kWh of electricity, worth US$835, and 0.75 t of CNT, worth around US$225,000 at current prices, and emit no CO_2.

In a conventional CCS system, around 7% of the electricity produced by a power station must be expended to regenerate the amine capture liquids, and energy is also expended in storing it, which does not happen in a CC CNF plant. In addition, companies making carbon nanotubes would avoid carbon tax charges.

"The CC CNF [plant] adds a high-temperature molten Li_2CO_3 electrolyser to a CC power plant design to remove exhaust CO_2 and transform it into a valuable carbon nanotube product. The present-day value of the carbon nanotubes product is around 10,000 times that of proposed, or in place, carbon tax costs of US$30/t, strongly incentivising CO_2 removal and spurring new public/private investment in this process to convert CO_2 into carbon nanotubes globally," the researchers conclude.

Energy Conversion and Management DOI: 10.1016/j.enconman.2016.06.007

Tailpipe to tank

Researchers are vying to use renewable energy to suck carbon dioxide out of the air and turn it back into fuel

By **Robert F. Service**

Stuart Licht has designed the ultimate recycling machine. The solar reactor that he and colleagues built in his lab at George Washington University in Washington, D.C., takes carbon dioxide (CO_2) from the atmosphere—a byproduct of fossil fuel combustion—and uses the energy in sunlight to turn it back into fuel. There are a few steps in between. Water is also involved in the reaction, which produces hydrogen (H_2) and carbon monoxide (CO); they in turn can be stitched into liquid hydrocarbon fuels. But Licht's is one of the most efficient devices of its type ever constructed.

It is only one of the solar fuel technologies taking shape in labs around the world. They embody a dream: the prospect of one day bypassing fossil fuels and generating our transportation fuels from sunlight, air, and water—and in the process ridding the atmosphere of some of the CO_2 that our fossil fuel addiction has dumped into it.

These schemes are no threat to the oil industry yet. In Licht's device, parts of the reactor run at temperatures approaching 1000°C, high enough to require specialized materials to hold the components. Other researchers are pursuing an alternative approach, developing catalysts that could carry out the same chemical reactions at or near room temperature, using electricity from sunlight or other renewables to power the chemical knitting process.

The bigger hurdle is economic. Oil is cheap, for the moment, and there is little incentive to adopt cutting-edge, costly alternatives. But the relentless march of climate change, and the elegance of the concept, have drawn researchers around the globe to the pursuit of solar fuels. "This is a very hot area right now," says Omar Yaghi, a chemist at the University of California (UC), Berkeley. And as Licht's reactor demonstrates, the research is making progress. "We're not there yet, but we're moving in the right direction," says Andrew Bocarsly, a chemist

ILLUSTRATION: TANG YAU HOONG

Published by AAAS

at Princeton University who is developing low-temperature catalysts.

Enthusiasts even see a glimmer of hope for making the technology economical: the steady spread of renewable electricity sources, such as wind farms and solar plants. Already, windmills and solar cells sometimes generate more power than locals can absorb. If this oversupply could be stored in chemical fuels, experts argue, utility providers might be able to save their power for use anytime and anywhere—and make extra money on the side.

THE NEED FOR LIQUID FUELS is unlikely to go away despite concerns about climate change. The high energy density and ease of transport of gasoline and other liquid hydrocarbons have made them the mainstay of the world's transportation infrastructure. Researchers continue to pursue the use of low-carbon gases, such as methane and hydrogen, as transportation fuels, and electric cars are proliferating. But for long-distance trucks and other heavy vehicles, as well as aviation, there is no good alternative to liquid fuels. Solar fuel proponents argue that finding a way to brew them from readily available compounds such as water and CO_2 could make a sizable dent in future CO_2 emissions.

The task essentially boils down to running combustion in reverse, injecting energy from the sun or other renewables into chemical bonds. "It's a very challenging problem, because it's always an uphill battle," says John Keith, a chemist at the University of Pittsburgh in Pennsylvania. It's what plants do, of course, to make the sugars they need to grow. But plants convert only about 1% of the energy that hits them into chemical energy. To power our industrial society, researchers need to do far better. Keith likens the challenge to putting a man on the moon.

The trouble is that CO_2 is a very stable, unreactive molecule. Chemists can force it to react by pumping in electricity, heat, or both. The first step in this process is usually ripping off one of CO_2's oxygen atoms to make CO. That CO can then be combined with H_2 to make a combination known as syngas, which can be converted into methanol, a liquid alcohol that can be either used directly or converted into other valuable chemicals and fuels. Massive chemical plants do just that, but they make their syngas not from air, but from plentiful and cheap natural gas. So the challenge for chemists is to create syngas from renewables more cheaply than current sources can match.

Licht, who calls his solar-generated mixture of CO and H_2 "sungas," says he's taking aim at that challenge by using both heat and electricity from the sun. His setup, which he details in a paper accepted at *Advanced Science*, starts with a high-end commercially available solar cell called a concentrated photovoltaic. It focuses a broad swath of sunlight onto a semiconductor panel that converts 38% of the incoming energy into electricity at a high voltage. The electricity is shunted to electrodes in two electrochemical cells: one that splits water molecules and another that splits CO_2. Meanwhile, much of the remaining energy in the sunlight is captured as heat and used to preheat the two cells to hundreds of degrees, a step that lowers the amount of electricity needed to split water and CO_2 molecules by roughly 25%. In the end, Licht says, as much as 50% of the incoming solar energy can be converted into chemical bonds.

It's unclear whether that process will produce syngas that's as cheap as that made from natural gas. But Licht notes that a 2010 economic analysis of his solar water splitting setup alone, which he first described in 2002, concluded that his approach could generate a kilogram of H_2—the energy equivalent of 4 liters of gasoline—at a cost of $2.61.

Yet it may be hard for Licht's sungas setup to lower the price further. Licht's charge-conducting electrolyte uses lithium, a somewhat rare and costly metal whose limited supplies could prevent a massive scale-up. Licht also faces competition from other researchers who also use high temperatures to ease the splitting of water and CO_2, but rely entirely on electricity instead of solar heating. But like sungas, those schemes, called solid oxide electrolysis cells, face the longevity challenges of running at high temperatures.

GIVEN THESE HURDLES, Bocarsly and others continue to try to split CO_2 at lower temperatures. One such approach is already commercial. In Iceland, a company called Carbon Recycling International opened a plant in 2012 that uses renewable energy to create syngas. The company harnesses the island's abundant geothermal energy to produce electricity, which drives electrolysis machines that split CO_2 and water. The resulting syngas is then turned into methanol.

Of course, most regions of the globe lack Iceland's abundant geothermal power needed to drive the process, so researchers are hunting for new catalysts that can split CO_2 with less energy. These catalysts typically sit on the cathode, one of two electrodes in an electrolytic cell containing water. At the opposite electrode, water molecules are split into electrons, protons, and oxygen, which bubbles away. The electrons and protons pass to the cathode, where CO_2 molecules split into CO and oxygen atoms that combine with the electrons and protons to make more water.

Today, the gold standard for such catalysts is, well, gold. In the 1980s, Japanese researchers found that electrodes made from gold had the highest activity for splitting CO_2 to CO of all the low-temperature setups. Then in 2012, Matthew Kanan, a chemist at Stanford University in Palo Alto, California, and colleagues discovered something even better: Making their electrode from a thin layer of gold divided into nanosized crystallites, they reported in the *Journal of the American Chemical Society*, slashed the electricity needed by more than 50% and increased the catalyst's activity 10-fold. The boundaries between the gold crystallites appear to promote the reaction.

At some $36,000 per kilogram, gold is still far too expensive for use on a mas-

Powered by geothermal energy, this plant in Iceland turns carbon dioxide into syngas and ultimately methanol fuel.

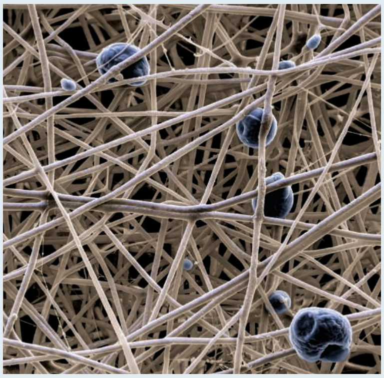
PHOTO: CARBON RECYCLING INTERNATIONAL

Conjuring chemical cornucopias out of thin air

By **Robert F. Service**

A fill-up at the gas station may seem expensive, but fuels are relatively cheap commodities. So would-be makers of solar fuels are looking for ways to apply their technology to making more valuable materials.

Last month, for example, Stuart Licht, a chemist at George Washington University in Washington, D.C., and colleagues reported in *Nano Letters* that they had developed a version of their solar reactor technology (see main story, p. 1158) that can take CO_2 out of the air and convert it into solid carbon nanofibers. The researchers found that when they added trace amounts of either nickel, copper, cobalt, or iron to their electrolysis cell, the metals form tiny islands on the cathode that then serve as landing sites for thousands of split-off carbon atoms to insert themselves and quickly grow into long, thin fibers. Licht's team had previously shown they could turn CO_2 into a solid carbon material called amorphous carbon, which is worth some $1000 per metric ton. But carbon nanofibers could be worth far more, perhaps as much as $25,000 per metric ton, because they are widely used in making lightweight, high-strength composites for applications such as car bumpers and airplane parts. "We are making a valuable commodity that we hope will produce a driving force for using this technology," Licht says.


Pricey carbon nanofibers can be made from CO_2.

Others are pursuing the same strategy. A small New Jersey–based company called Liquid Light is working to commercialize technology for converting CO_2 into ethylene glycol, a commodity chemical with a $27 billion annual market. Another company, Skyonic, recently opened a demonstration plant in Texas that turns CO_2 into baking soda, hydrochloric acid, and bleach.

Such commodities aren't manufactured on a scale anywhere near that of gasoline and other transportation fuels. So making them with CO_2 siphoned off a smokestack or pulled from the air isn't likely to make a sizable impact on global atmospheric CO_2 levels, says Matthew Kanan, a chemist at Stanford University in Palo Alto, California, who is working to convert CO_2 into plastics and other higher value commodities. However, he says, "Perhaps we can use that as a stepping stone." With time and experience, companies may then find way to improve their processes, lower their costs, and begin to make high-volume, low-cost compounds such as fuels. "I'm a technology optimist," Kanan says. ■

sive scale. Last year, however, researchers led by Feng Jiao, a chemist at the University of Delaware (UD), Norwalk, reported in *Nature Communications* that catalysts made from silver nanoparticles do almost as well. And this year, they reported in *ACS Catalysis* that even cheaper catalysts made from tiny zinc spikes called dendrites are also proving highly effective at churning out CO.

Catalysts that could be even cheaper are in the works. Researchers at UC Berkeley, for example, reported last month that they had made a highly porous crystalline material out of organic ring-shaped compounds with a combination of cobalt and copper atoms at their core. When layered atop an electrode and dunked in a water-based solution, the porous materials split CO_2 molecules into CO at a rate of 240,000 per hour—a furious pace compared with most other room-temperature catalysts. And last year, Kanan and his colleagues reported that electrodes made of nanocrystalline copper could bypass the need for syngas, allowing them to directly synthesize a variety of more complex liquid fuels, such as ethanol and acetate, at unprecedented efficiencies.

Researchers worldwide are also pursuing another rich vein: driving the low-temperature electrolysis of CO_2 and H_2O with energy directly from sunlight. Most efforts center on using light-absorbing semiconductors, such as titanium dioxide–based nanotubes, to churn out CO, methane, or other hydrocarbons. So far, such setups aren't very efficient; typically they convert less than 1% of the incoming solar energy into chemical bonds. Bocarsly and others have done better using the sun's ultraviolet light, which makes up only a tiny part of the spectrum. But at the American Chemical Society meeting in Boston last month, Joel Rosenthal, a chemist at UD Newark, reported that his team has developed a bismuth-based photocatalyst that converts 6.1% of incoming visible light energy to chemical bonds in CO.

Despite progress on all these fronts, Kanan cautions that solar fuels still have a long way to go to compete directly with liquid fossil fuels, especially now that the price of oil has fallen below $50 per barrel. And barring a concerted push from governments worldwide to cap or tax carbon emissions, solar fuels may never be able beat oil-derived fuels on cost alone. "It's a tall order," he says.

But Paul Kenis, a solar fuels researcher at the University of Illinois, Urbana-Champaign, argues that the broad penetration of solar and wind power offers hope. Denmark, for example, already produces some 30% of its electricity from wind farms and is on pace to reach 50% by 2020. On a particularly blustery day in July, the nation's wind turbines generated as much as 140% of the country's electrical requirements. The excess was sent to its neighbors, Germany, Norway, and Sweden. But the oversupply added to utilities' fears that in times of peak renewable power production, the value of electricity could fall to zero or even below, as producers would have to pay others to take it so as not to damage their grid.

That's where solar fuel producers could stand to benefit, Kenis says: By absorbing that power and using it to make fuels and other commodities, they could essentially act as energy banks and perhaps earn some cash as well. For now, Kanan argues, it still makes the most economic sense simply to shunt excess renewable power into the grid, displacing fossil energy. But someday, if renewable power becomes widespread enough and the technology for making renewable fuels improves, we may be able to guzzle gas without guilt, knowing we are just burning sunlight. ■

MATERIALS NEWS

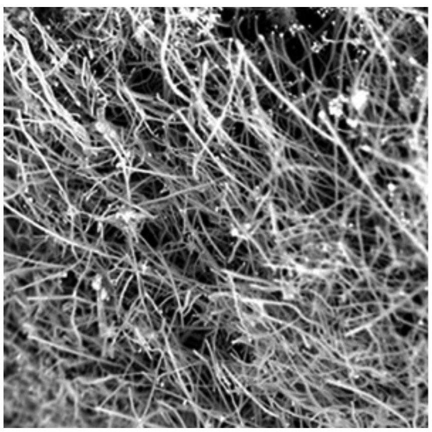
Researcher Demonstrates How to Suck Carbon from the Air, Make Stuff from It

A novel electrochemical process sequesters carbon in the form of a versatile building material.

By Mike Orcutt on August 19, 2015

A new method for taking carbon dioxide directly from the air and converting it to oxygen and nanoscale fibers made of carbon could lead to an inexpensive way to make a valuable building material—and may even serve as a weapon against climate change.

Carbon fibers are increasingly being used as a structural material on the aerospace, automotive, and other industries, which value its strength and light weight. The useful attributes of carbon fibers, which also include electrical conductivity, are enhanced at the nanoscale, says Stuart Licht, a professor of chemistry at George Washington University. The problem is that it's very expensive to make carbon fibers, much less nanofibers. Licht says his group's newly demonstrated technology, which both captures the carbon dioxide from the air and employs an electrochemical process to convert it to carbon nanofibers and oxygen, is more efficient and potentially a lot cheaper than existing methods.



The fibers in this microscope image are made of carbon, produced via a new method that also removes carbon dioxide from the air.

But it's more than just a simpler, less expensive way of making a high-value product. It's also a "means of storing and sequestering carbon dioxide in a useful manner, a stable manner, and in a compact manner," says Licht. He points out that if the process is powered by renewable energy, the result is a net removal of carbon dioxide from the atmosphere. In a recent demonstration, his group used a unique concentrated solar power system, which makes use of infrared sunlight as well as visible light to generate the large amount of heat needed to run the desired reaction.

The process requires molten lithium carbonate, with another compound, lithium oxide, dissolved in it. The lithium oxide combines with carbon dioxide in the air, forming more lithium carbonate. When voltage is applied across two electrodes immersed in the molten carbonate, the resulting reaction produces oxygen, carbon (which deposits on one of the electrodes), and lithium oxide, which can be used to capture more carbon dioxide and start the process again.

The researchers demonstrated the ability to make a variety of different nanofiber shapes and diameters by adjusting specific growth conditions, such as the amount of current applied at specific points of time and the composition of the various ingredients used in the process. They also showed they could make very uniform fibers. Licht says the mechanisms underlying the formation of the fibers still need to be better understood, and he's confident the group can keep developing more control over the nature of the fibers it makes.

As for the technology's emissions-cutting potential, the researchers are optimistic. They calculate that given an area less than 10 percent of the size of the Sahara Desert, the method could remove enough carbon dioxide to make global atmospheric levels return to preindustrial levels within 10 years, even if we keep emitting the greenhouse gas at a high rate during that period.

Of course, this would require a huge increase in demand for carbon nanofibers. Licht believes the material's properties, especially the fact that it is so lightweight and also very strong, will spur greater and greater use as the cost comes down, and he thinks his new process can help with that. Imagine that carbon fiber composites eventually replace steel, aluminum, and even concrete as a building material, he says. "At that point, there could be sufficient use of this that it's actually acting as a significant repository of carbon."

CHEMISTRY

New recipe produces ammonia from air, water, and sunlight

Catalytic approach could eliminate CO_2 emissions from the key step in making fertilizer

By **Robert F. Service**

The ability to turn the nitrogen in air into fertilizer has enabled farmers to feed billions more people than our planet could otherwise support. But it's costly. The massive chemical plants that produce ammonia—the starting material for fertilizer—consume up to 5% of the world's natural gas and belch out hundreds of millions of tonnes of carbon dioxide (CO_2) annually. Now, chemists have come up with an alternative approach drawing on renewable energy. On page 637, they report using heat and electricity produced from sunlight to stitch together nitrogen from the air and hydrogen from water to make ammonia, all without emitting a molecule of CO_2.

"It's an important scientific advance," says Morris Bullock, a chemist at the Pacific Northwest National Laboratory in Richland, Washington. Still, says Ellen Stechel, a chemical physicist at Arizona State University, Tempe, the question is whether the process's "very respectable" efficiency in the lab can be scaled up to compete with the current ammonia industry.

Nitrogen molecules in air are inert, held together by triple bonds that aren't easily broken. In the early 1900s, the German chemists Fritz Haber and Carl Bosch figured out how to make nitrogen more biologically reactive. They used high pressures and temperatures to sever those bonds and weld nitrogen atoms to hydrogen to make ammonia, NH_3. Today, that reaction produces hundreds of millions of tons of ammonia each year.

Yet the large amounts of energy required for this reaction have prompted a number of researchers to look for alternatives. One popular approach has been to search for catalysts that break nitrogen's triple bonds and make ammonia when fed electricity. So far, however, even the best such catalysts harness only about 1% of the electrons for forming ammonia's bonds.

Stuart Licht, a chemist at George Washington University in Washington, D.C., tackled the problem from the opposite direction. He spotted work on fuel cells that break down ammonia into nitrogen and hydrogen, generating electricity in the process. A new electrolyte, which helps charged ions move in the device, improved the efficiency of the fuel cell.

Licht and colleagues tried using the same electrolyte—a molten mixture of potassium and sodium hydroxide—in reverse to synthesize ammonia. It worked. In their reactor, they combined the electrolyte with catalytic nanoparticles made from iron oxide, then fed in water, air, heat, and electricity. The reactor split water, snapped nitrogen's strong bonds, and welded the components into ammonia and molecular hydrogen (H_2)—itself a fuel. All told, 65% of the electricity wound up stored in chemical bonds: 35% in ammonia and 30% in H_2 molecules.

Though impressive, the result "still has a long way to go" to replace the Haber-Bosch process, says James Miller, a chemist at Sandia National Laboratories in Albuquerque, New Mexico, who specializes in using solar energy to make chemical fuels. The reactor is most efficient when fed only a trickle of electricity. Licht and his team will need to boost the current 50-fold to match related industrial processes, Stechel says. Still, Miller adds, "he's on the right track." ■

A vital chemical with major costs

120

Millions of tons of N_2 extracted from air annually to produce ammonia for fertilizer

2

Percentage of world energy used for ammonia production

102

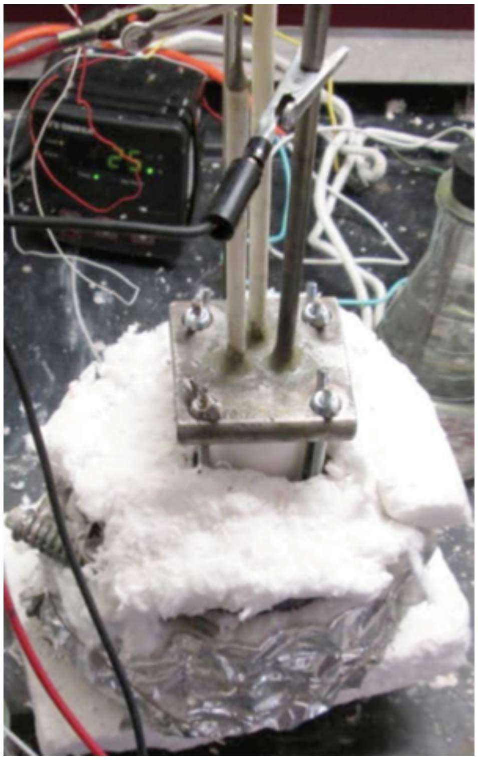
Billion dollars, the estimated market for ammonia in 2019

Published by AAAS

chemistryworld ROYAL SOCIETY OF CHEMISTRY

Low-emission ammonia offers food and climate solution

7 August 2014 **Andy Extance**



Stuart Licht's team is working on new ammonia production technology in its 'Solar Thermal Electrochemical Production' approach © AAAS

Chemists in the US have discovered a low cost way to make ammonia that could help feed the world's growing population without contributing to global warming. **Stuart Licht**'s team at George Washington University in Washington, DC, has produced **ammonia directly from electricity, air and steam**. 'Unlike the conventional process, which has a massive carbon footprint, this produces ammonia for fertiliser without CO_2 emissions,' says Licht.

Ammonia has transformed our world, helping grow more food, but also adding greenhouse gases. **Developed in the early 20th century** and still dominant, the Haber process produces it by reacting nitrogen – the major constituent of Earth's air – with hydrogen using a catalyst like iron. That takes high temperatures and pressures, using around 2% of the world's energy. Today the hydrogen comes from reacting methane – around 3-5% of the total consumed – with steam, which also produces vast amounts of carbon dioxide.

In recent years Licht's team has developed 'Solar Thermal Electrochemical Production' (STEP), avoiding CO_2 emissions in various processes, such as **cement** and **iron** manufacturing. One part of this work has been producing hydrogen from water by passing electrical current through molten salts like sodium hydroxide. Licht then read about a fuel cell made by **Jason Ganley** at Colorado School of Mines that generated electricity by reacting ammonia with air in molten hydroxide. The George Washington researchers first tried simply reversing that cell, without success. 'A key to ammonia production was the addition of nano-iron oxide,' Licht says.

Whereas previous attempts based on electrolysing water and air converted less than 1% of the electricity used to ammonia, the new approach converts 35%. 'Less than 100% efficiency is not necessarily a loss to the process,' Licht stresses. 'In this case you consume current to co-generate hydrogen, which is a useful fuel.' However, the iron oxide catalyst clumped together after a few hours' use, dramatically reducing the cell's efficiency, although Licht's team is already preparing to publish a more stable design.

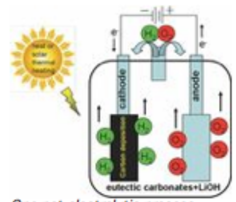
As well as avoiding direct CO_2 emissions by getting hydrogen from steam not methane, energy consumption is two-thirds that of the Haber process. Licht expects to reduce this further and has also incorporated the approach into a system exploiting thermal energy collected from the Sun.

Ganley, who has previously worked with Licht but not on this study, says it could have 'far-reaching benefits'. 'The electrolyte is very inexpensive and highly conductive, and the reactants are carbon-free,' he explains.

Green Car Congress
Energy, technologies, issues and policies for sustainable mobility

GWU team uses one-pot process to co-generate H2 and solid carbon from water and CO2; solar fuels

30 December 2014

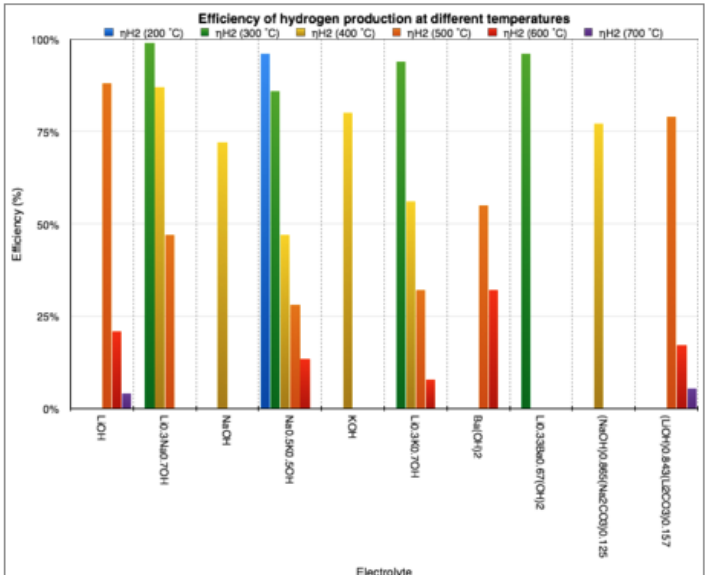


One-pot electrolytic process produces H_2 and solid carbon from water and CO_2. Li et al. Click to enlarge.

A team at George Washington University led by Professor Stuart Licht has simultaneously co-generated hydrogen and solid carbon fuels from water and CO_2 using a mixed hydroxide/carbonate electrolyte in a "single-pot" electrolytic synthesis at temperatures below 650 °C. The work is a further development of their work with STEP (solar thermal electrochemical process)—an efficient solar chemical process, based on a synergy of solar thermal and endothermic electrolyses, introduced by Licht and his colleagues in 2009. (Earlier post, earlier post.) (In short, STEP uses solar thermal energy to increase the system temperature to decrease electrolysis potentials.)

Licht and his colleagues over the past few years have delineated the solar, optical, and electronic components of STEP. In this study, they focused on the electrolysis component for STEP fuel, producing hydrogen and graphitic carbon from water and carbon dioxide. A paper on the new work is published in the journal *Advanced Energy Materials*.

Molten hydroxides are important as conductive, high-current, low-electrolysis-potential electrolytes for water splitting to generate hydrogen, the team notes in the paper. The Coulombic efficiency of electrolytic water splitting, η_{H2} (moles H_2 generated per 2 Faraday of applied charge), approaches 100% in low melting point, mixed alkali molten hydroxides at temperatures up to 300 °C.



Measured coulombic efficiency of hydrogen generation (η_{H2}) in various molten hydroxide electrolytes at various temperatures. Data source: Li *et al.* Click to enlarge.

In the study, they achieve the synthesis of hydrogen and carbon fuel using a mixed, hydroxide/carbonate electrolyte, nickel anode (generating O_2), and nickel or steel cathode (generating graphite and hydrogen). Low hydroxide fractions in the electrolyte ensure efficient carbon formation, while high fractions form only H_2 at the cathode; added barium and lithium salts ensure effective nickel anode stability.

> *The general use of solar thermal energy to lower the potential of useful electrolyses can be applied to liquid, gas, or solid phase electrolyte cells. In general, we have found an energy advantage in applying STEP to liquid, molten electrolyte cells. Such cells can be driven by thermal sunlight to high temperature accommodating both facile kinetics at high current density and a lower endothermic electrolysis potential. Importantly, molten salt cells can often accommodate high reactant concentrations, which lead to a further decrease in the electrolysis potential … We have previously demonstrated molten hydroxide electrolytes for solar water splitting to hydrogen fuel, and molten carbonate electrolytes for solar carbon dioxide splitting to carbon and carbon monoxide fuels.*
>
> *… In this study, we focus on the electrolysis component for STEP fuel. Specifically, we present the first molten electrolyte sustaining electrolytic co-production of both hydrogen and carbon products in a single cell.*
>
> *… We demonstrate here the functionality of new lithium–barium–calcium hydroxide carbonate electrolytes to co-generate hydrogen and carbon fuel in a single electrolysis chamber at high current densities of several hundreds of mA/cm^2, at low electrolysis potentials, and from water and CO_2 starting points, which provides a significant step towards the development of renewable fuels.*
>
> —Li *et al.*

The one-pot co-synthesis of hydrogen and carbon and C was carried using a new $Li_{1.6}Ba_{0.3}Ca_{0.1}CO_3$ electrolyte with LiOH as hydroxide component. The synthesis has high coulombic efficiency with ≈62% of the current generating H_2 and 20% generating carbon at an applied electrolysis current of 2 A through the 3.75 cm^2 planar nickel anode and nickel cathode.

The authors noted that the H_2 Coulombic efficiency in the $LiOH/Li_{1.6}Ba_{0.3}Ca_{0.1}CO_3$ electrolyte was higher than that observed at 500 °C in a pure barium hydroxide electrolyte, and which had not permitted the co-generation of fuels.

Resources

- Li, F.-F., Liu, S., Cui, B., Lau, J., Stuart, J., Wang, B. and Licht, S. (2014), "A One-Pot Synthesis of Hydrogen and Carbon Fuels from Water and Carbon Dioxide," *Adv. Energy Mater.* doi: 10.1002/aenm.201401791

technology review
Published by MIT

ENERGY

New Cement-Making Method Could Slash Carbon Emissions

The proof-of-concept device concentrates sunlight to break apart limestone.

FRIDAY, MAY 11, 2012 | BY KEVIN BULLIS

Researchers at George Washington University have bolted together an ungainly contraption that they say efficiently uses the energy in sunlight to power a novel chemical process to make lime, the key ingredient in cement, without emitting carbon dioxide. The device puts to work about half of the energy in sunlight (solar panels, in comparison, convert just 15 percent of the energy in sunlight into electricity).

Cement production alone emits 5 to 6 percent of total man-made greenhouse gases, and most of that comes from producing lime. Some of the greenhouse-gas emissions from conventional cement production come from using fossil fuels to heat up limestone to high temperatures—about 1,500 °C. Replacing fossil fuels with renewable energy is straightforward, but not necessarily economical. The new work focuses on a harder problem. About 60 percent of the carbon-dioxide emissions from cement production is inherent to the process. Lime is made by heating up limestone—that is, calcium carbonate—until it releases carbon dioxide.

The new process changes the chemistry. Rather than emitting carbon dioxide, it converts the gas, using a combination of heat and electrolysis to produce oxygen and either carbon or carbon monoxide, depending on the temperatures employed. Both carbon and carbon monoxide are useful products that might otherwise have been made using fossil fuels.

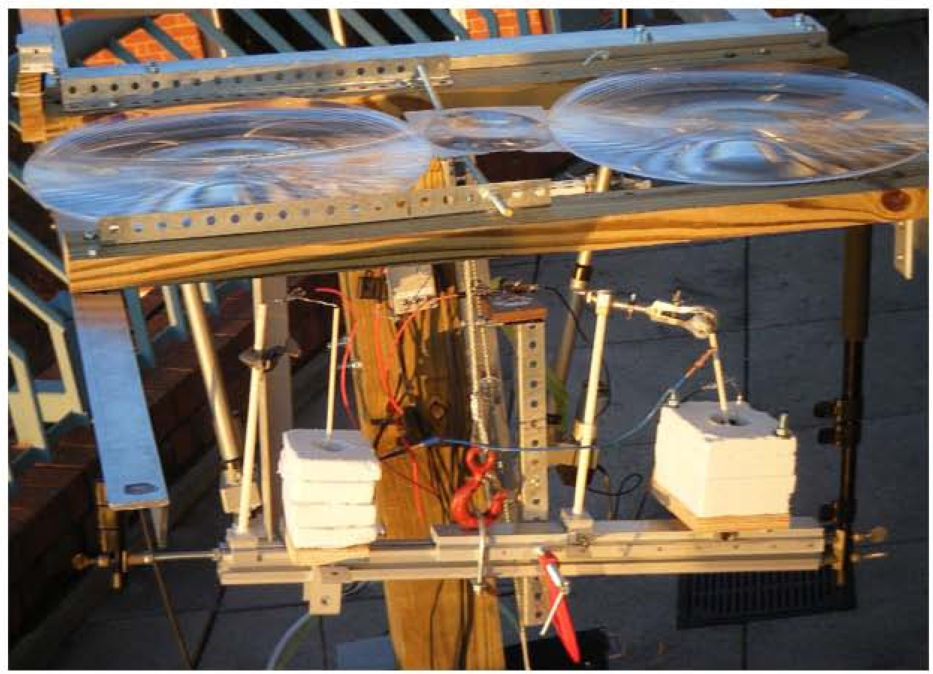
To make the electrolysis practical, the researchers mixed solid calcium carbonate with liquid lithium carbonate, which is molten at the temperatures that are optimal for the process—about 900 °C. The liquid form is conducive to electrolysis. The elevated temperatures lower the amount of electricity needed to electrolyze, and cause the lime to precipitate out of the mixture, making it easy to collect. (At lower temperatures, the lime is more soluble, so it doesn't precipitate.)

To demonstrate the process, the researchers built a device that includes three Fresnel lenses for concentrating sunlight. Two of those heat up the mixture of lithium carbonate and limestone. Those are the largest lenses. Their relative size reflects the fact that most of the energy needed for the process goes to heating up the mixture. The third, smaller lens focuses light on a high-efficiency solar cell, which provides the relatively small amount of electricity needed to electrolyze the hot carbonate mixture.

The device is just a proof of concept, not ready for commercialization. It's small, and it works only when it's sunny—and intermittent operation isn't ideal for an industrial process. The researchers propose using molten salt to store heat, a system used in some solar thermal power plants. That would allow the process to run day and night. The electricity could come from using the heat to generate steam to spin a turbine, as in a solar thermal power plant, or from any other source of electricity.

Stuart Licht, the professor of chemistry at George Washington University who led the work, estimates that the process, if it can be scaled up, could be cheaper than conventional lime production. He says it's more efficient than solar panels because it uses parts of the solar spectrum that solar cells can't efficiently convert into electricity.

The process still requires a lot of energy, says C12 Energy CEO Kurt House, who has developed low-carbon concrete production processes. "It comes down to how you want to use solar energy," he says. "If the efficiency is as good as they say it is, then I agree, this is very, very interesting. But I'm skeptical."



Rock splitter: Two large, Fresnel lenses concentrate sunlight to heat limestone up to 900 °C. A smaller lens concentrates light onto a small solar cell that generates enough electricity to break apart limestone, forming lime for cement, along with oxygen and graphite. Stuart Licht

Zero Carbon Cement Production with Solar Thermal

APRIL 10, 2012 BY SUSAN KRAEMER

In a study published in a recent issue of *Chemical Communications*, a team of researchers from Virginia's George Washington University explain a revolutionary way to make lime cement that releases zero CO_2 emissions – and costs less too.

The researchers' rough analysis shows that the total cost of the limestone material, solar heat and electricity is $173 per ton of lime and 0.786 tons of carbon monoxide (0.786 tons of carbon monoxide are produced for every ton of lime).

The market value of carbon monoxide is $600 per ton, or $471 per 0.786 tons. So after selling the carbon monoxide, the cost of the lime production is actually a negative number. $173 – $471 = minus $298 per ton.

No carbon emissions. Cheap. And even better, it has wide applications.

Nearly all of the other heaviest emitters could similarly be stripped of their greenhouse gas problem with this technology, the scientists say.

(Among other industries, these industrial processes include purifying iron and aluminum, making glass, paper, sugar, and agriculture, cleaning smoke stacks, softening water, and removing phosphates from sewage.)

The next step would be is simply scaling up the fairly straightforward process for commercialization. "Although the process itself is entirely new" coauthor Stuart Licht, a chemistry professor at George Washington University, told *Phys.org*."the individual components (solar towers, 24/7 operation storing solar energy with molten salts) are already in place. Solar energy can be used to efficiently make products without carbon dioxide, and at solar energy efficiencies higher than in photovoltaics."

The timing is perfect: a burgeoning Asia is about to build the new mega cities of the 21st century. And super hot solar thermal heat is ready: Halotechnics Molten Glass Thermal Storage Could Mean 6 Cent Solar.

In the electrolysis process alone, even without solar power, but using fossil heat source, "worst case scenario" says Licht, "the products are lime, graphite and oxygen; there is still no CO_2 product, but CO_2 would be used in the energy to drive the process."

Stuart Licht, et al. "STEP Cement: Solar Thermal Electrochemical Production of CaO without CO2 emission." *Chem. Commun.*, DOI: 10.1039/C2CC31341C

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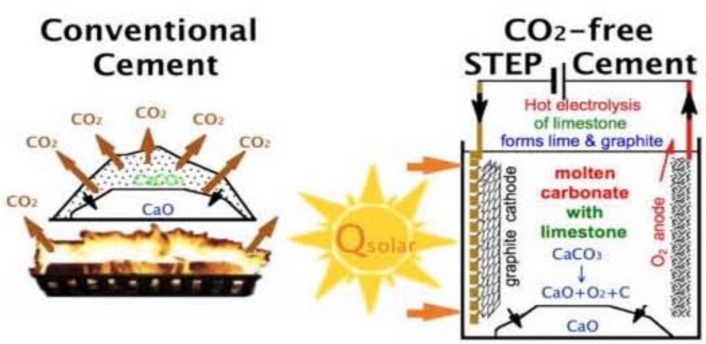

In the conventional production of lime from limestone, fossil fuels are burned during the decarbonation process, resulting in a carbon dioxide byproduct. In the STEP process, solar thermal energy is used to heat the limestone as well as assist in electrolysis, producing a different chemical reaction with no carbon dioxide byproduct. Image credit: Licht, et al. ?2012 The Royal Society of Chemistry

(Phys.org) -- While the largest contributor to anthropogenic greenhouse gas emissions is the power industry, the second largest is the more often overlooked cement industry, which accounts for 5-6% of all anthropogenic CO_2 emissions. For every 10 kg of cement produced, the cement industry releases a full 9 kg of CO_2. Since the world consumes about 3 trillion kg of cement annually, this sector has one of the highest potentials for CO_2 emission reductions. But while processes are being explored to sequester the CO_2 from cement production, so far no process can completely eliminate it.

Jumping on this opportunity for improvement, a team of researchers from George Washington University in Ashburn, Virginia, has developed a method for cement production that releases zero CO2 emissions. In addition, the scientists estimate that the new production process will be cheaper than the existing process used in the cement industry.

In their study published in a recent issue of Chemical Communications, the scientists describe the process as the Solar Thermal Electrochemical Production of cement, or STEP cement. (The team previously used a similar STEP process for carbon capture, with the potential for decreasing CO2 levels in the atmosphere to pre-industrial levels.)

As the scientists explain, 60-70% of CO2 emissions during cement production occurs during the conversion of limestone into lime. This conversion involves decarbonation, or removing the carbon atom and two oxygen atoms in limestone (CaCO3) to obtain lime (CaO) with CO2 as the byproduct. The remainder of the emissions comes from burning fossil fuels, such as coal, to heat the kiln reactors that produce the heat required for this decarbonation process.

The STEP process addresses both issues, starting by replacing the fossil fuel heat source with solar thermal energy. The solar heat is not only applied directly to melt the limestone, it also provides heat to assist in the electrolysis of the limestone. In electrolysis, a current applied to the limestone changes the chemical reaction so that instead of separating into lime and CO2, the limestone separates into lime and some other combination of carbon and oxygen atoms, depending on the temperature of the reaction. When electrolyzed below 800°C, the molten limestone forms lime, C, and O2. When electrolyzed above 800°C, the product is lime, CO, and ?O2.

"Electrolysis changes the product of the reaction of the limestone as it is converted to lime," coauthor Stuart Licht, a chemistry professor at George Washington University, told Phys.org. "Rather than producing carbon dioxide, it reduces the carbon dioxide (adds electrons) and produces only oxygen and graphite (which can be readily stored as solid carbon) or CO for fuels, plastics or pharmaceuticals. This is accomplished at low energy and high throughput."

When separated, the carbon and oxygen atoms no longer pose the threat to the atmosphere that they do as CO2. As Licht explained, the carbon monoxide byproduct in the higher temperature reaction can be used in other industries, such as to produce fuels, purify nickel, and form plastics and other hydrocarbons. Plus, the carbon monoxide is produced significantly below market value by this solar thermal electrolytic process. The main product, lime, doesn't react with the other byproducts, but instead forms a slurry at the bottom of the vessel where it can easily be removed.

"This study presents a low-energy, entirely new synthetic route to form CaO without any carbon dioxide emission, and is based on unexpected solubility behavior in molten salts," Licht said. "This synthesis can be accomplished without solar energy, and without our new STEP process, but is particularly attractive when combined with this new solar process. Alternatively, the new synthesis could be used by industry to produce cement using any non-solar renewable or nuclear energy without any CO2 release, or greatly decrease CO2 if fossil fuels were used to drive the new cement production (in the latter, worst-case scenario, the products are lime, graphite and oxygen; there is still no CO2 product, but CO2 would be used in the energy to drive the process)."

According to the researchers, the STEP process can be performed at a lower projected cost than the existing cement industry process. In fact, when accounting for the value of the carbon monoxide byproduct, the cost of the lime production is actually negative. The researchers' rough analysis shows that the total cost of the limestone material, solar heat, and electricity is \$173 per ton of lime and 0.786 tons of carbon monoxide (0.786 tons of carbon monoxide are produced for every ton of lime). The market value of carbon monoxide is \$600 per ton, or \$471 per 0.786 tons. So after selling the carbon monoxide, the cost of the lime production is \$173 - \$471 = -\$298 per ton. For comparison, the cost to produce lime in the conventional way is about \$70 per ton. The researchers emphasize that this analysis is not comprehensive, but it indicates the cost benefit of STEP cement, not even considering the value of eliminating CO2 emissions.

The scientists add that the STEP process could be extended beyond cement production to other applications that convert limestone to lime, such as purifying iron and aluminum; producing glass, paper, sugar, and agriculture; cleaning smoke stacks; softening water; and removing phosphates from sewage.

The next challenge for the researchers lies in scaling up the process for commercialization. They note that Gemasolar, a large-scale solar thermal plant, is already in operation. Other solar thermal plants are following, with electricity costs expected to decrease. To maintain constant operation, molten salt storage of the thermal energy can allow production to continue even during fluctuations in sunlight and at night. Another issue may be finding enough lithium carbonate for the electrolyte, although the metal is not consumed in the STEP process and so is not a recurring cost.

"We plan to scale up the outdoor STEP cement prototype, and in general want to increase the portfolio of useful chemicals made by our new solar process," Licht said. "The goals are to replace today's fossil fuel economy with a renewable chemical economy. Scale-up is the challenge. Although the process is entirely new, the individual components (solar towers, 24/7 operation storing solar energy with molten salts) are already in place. Solar energy can be used to efficiently make products without carbon dioxide, and at solar energy efficiencies higher than in photovoltaics."

More information: Stuart Licht, et al. "STEP Cement: Solar Thermal Electrochemical Production of CaO without CO2 emission." Chem. Commun., DOI: 10.1039/C2CC31341C

http://phys.org/news/2012-04-solar-thermal-cement-carbon-dioxide.html

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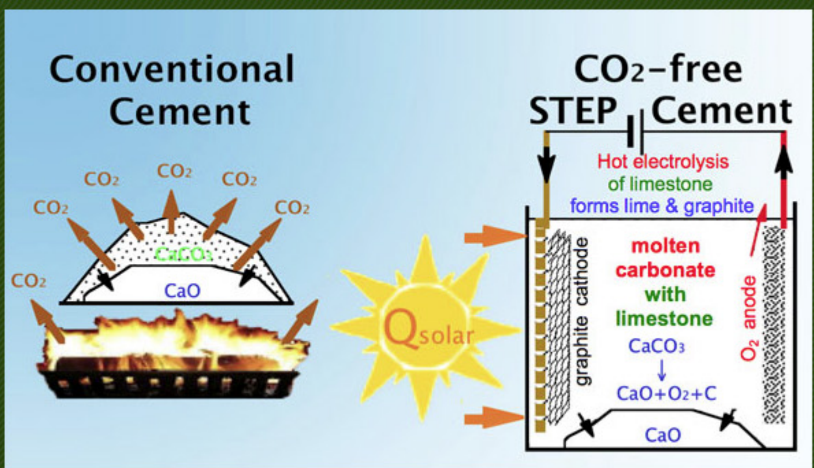
Solar-powered cement production without carbon dioxide emissions

The global cement industry is currently one of the largest single emitter of carbon dioxide, generating on average about 830 kg of this greenhouse gas for each 1000 kg of cement produced (source: International Energy Agency 2007, Tracking Industrial Energy Efficiency and CO2 Emissions; pdf). Considering that the worldwide annual production of cement is a whopping 3.8 trillion kg (source), the cement industry alone accounts for approximately 5-6% of man-made CO2 emissions.

In a previous Nanowerk Spotlight ("New solar-powered process removes CO2 from the air and stores it as solid carbon") we introduced a novel solar conversion process, combining electronic and chemical pathways, for carbon dioxide capture. This STEP (Solar Thermal Electrochemical Production) process proactively converts anthropogenic carbon dioxide generated in burning fossil fuels, as well as eliminates carbon dioxide emissions associated with the generation of metals and bleach. In a subsequent Spotlight ("Reinventing iron production using clean renewable energy instead of coal") we showed how the STEP process could be used as an effective new carbon-dioxide-free process for iron production.



Conventional thermal decomposition production of lime (left) versus STEP direct solar conversion of calcium carbonate to calcium oxide (right) eliminating CO2. (Photo source: Dr. Licht, University of Washington)

The research team, led by Stuart Licht, a professor of chemistry at George Washington University, has now presented a solar-powered process to produce cement without any carbon dioxide. In a paper (accepted manuscript) in the April 5, 2012 online edition of Chemical Communications ("STEP Cement: Solar Thermal Electrochemical Production of CaO without CO2 emission"), they show that STEP-produced cement operates at solar energy conversion efficiencies higher than that in any solar photovoltaic.

"In cement production, the majority of CO2 emissions occurs during the decarbonation of limestone (CaCO3) to lime (CaO) and the remainder (30 to 40%) from burning fossil fuels, such as coal, to heat the kiln reactors to ~900°C," Licht explains to Nanowerk. " Our study presents a low-energy, entirely new synthetic route to form CaO without any carbon dioxide emission, and is based on unexpected solubility behavior in molten salts. This synthesis can be accomplished without solar energy, and without our new STEP process, but is particularly attractive when combined with this new solar process."

"Alternatively" he adds, "the new synthesis could be used by industry to produce cement using any non-solar, renewable or nuclear energy without any CO2 release, or greatly decrease CO2 if fossil fuels were used to drive the new cement production – in the latter, worst case scenario, the products are lime, graphite and oxygen; there is still no CO2 product, but CO2 would be used in the energy to drive the process."

In STEP cement limestone undergoes low energy electrolysis to produce lime, O2 and reduced carbonate without carbon dioxide emission.

"There have been proposals to form cement which recaptures or sequesters some of the CO2 emitted during its production process" says Licht. "This, however, is the first process which forms no CO2 while producing cement."

In this new technique, the kiln limestone-to-lime process is replaced by an electrolysis process which changes the product of the reaction of the limestone as it is converted to lime. Rather than producing carbon dioxide, it reduces the carbon dioxide (adds electrons) and produces only oxygen and graphite (which can be readily stored as solid carbon) or CO for fuels, plastics or pharmaceuticals. This is accomplished at low energy and high throughput.

The researchers plan to scale up the outdoor STEP cement prototype and in general want to increase the portfolio of useful chemicals made by their new solar process.

"The goals are to replace today's fossil fuel economy with a renewable chemical economy," says Licht. "It works fine in the lab but scale-up is the challenge."

He points out that, although the process is entirely new, the individual components –solar towers, 24/7 operation storing solar energy with molten salts – are already in place.

The bottom line of these research results is that solar energy can be used to efficiently make products without carbon dioxide, and at solar energy efficiencies higher than in photovoltaics.

architects newsdesk

Solar Thermal STEP Method Could Make Cement Production Greenhouse Gas-Free

Tue, 10/04/2012 - 17:46

The cement manufacturing process has a staggering carbon footprint – said to be responsible for up to 7 percent of global greenhouse gas emissions, the industry releases around 9 lbs of carbon dioxide for every 10 lbs of cement produced. With global production standing at around three billion tonnes each year, there remains a huge need to find a greener method of production. While there have been various efforts in recent years, researchers at George Washington University have devised the first technique, called Solar Thermal Electrochemical Production (STEP), to completely eliminate CO2 emissions from the process, and it would even be cheaper than current methods of production.

http://pedro.co.za/node/4772

Step up for green iron production

09 September 2010

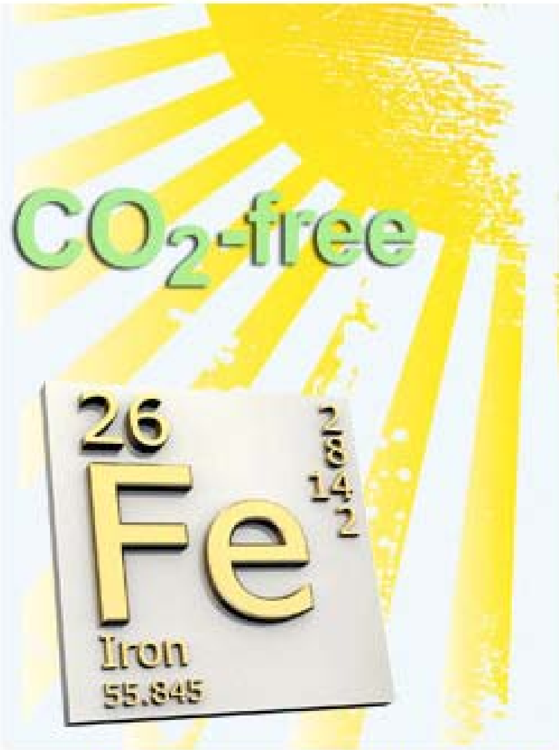
Highlights in Chemical Technology

Chemical technology news from across RSC Publishing.

A more environmentally friendly way of producing iron developed by scientists in the US and China could reduce industrial carbon dioxide emissions by a quarter worldwide.

Since the beginning of the industrial revolution, iron metal has been produced by melting iron ore at temperatures over 2000°C in a blast furnace. This produces large amounts of CO_2, which is released into the atmosphere and contributes to climate change.

The new method developed by Stuart Licht at George Washington University in Washington, DC and Baohui Wang at Northeast Petroleum University in Daqing could result in completely CO_2-free iron production. The team show that iron ores (Fe_2O_3 and Fe_3O_4) can be dissolved in molten lithium carbonate at temperatures of around 800°C - a process that was previously thought impossible. Adding an electrical current to the molten mix separates the iron ore into its component parts, iron and oxygen, which can be collected by two electrodes in the solution.



Global carbon dioxide emissions could be cut by a quarter

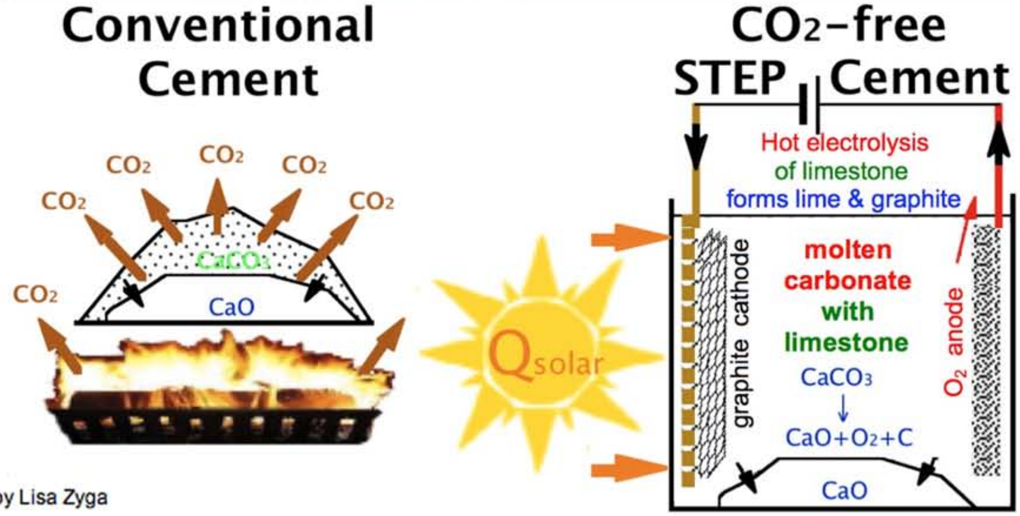
Less energy is required to generate the lower temperatures and power the electrolysis, but Licht also demonstrates that these can be achieved using renewable energy. The team employ their recently developed solar technique, called solar thermal electrochemical photo (Step) - which uses the Sun's thermal energy to melt the lithium carbonate solution while the visible light energy powers the electrolysis. Using the Step process no CO_2 is produced.

'Step production of iron would be cost effective, and could allow iron production facilities to be housed in new geographic locations, such as in closer to urban centres or in high sunlight geographies,' says Licht, as well as eliminating one of the major contributors to global carbon dioxide emission.

Neal Woodbury, a renewable energy expert at Arizona State University, US, comments 'if the Step process can be performed at industrial scale, it holds considerable promise. Of particular note is that it should be possible to utilise waste heat from the processes that produce the required electricity, thus decreasing the energy input as well.'

Licht has previously shown that the Step technology can be used for carbon capture and for generating hydrogen fuel. And says he sees the scale-up of CO_2-free iron production from the laborartory to industry as an exciting challenge.

Emma Shiells



April 10, 2012 by Lisa Zyga

In the conventional production of lime from limestone, fossil fuels are burned during the decarbonation process, resulting in a carbon dioxide byproduct. In the STEP process, solar thermal energy is used to heat the limestone as well as assist in electrolysis, producing a different chemical reaction with no carbon dioxide byproduct. Image credit: Licht, et al. ©2012 The Royal Society of Chemistry

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The STEP process addresses both issues, starting by replacing the fossil fuel heat source with solar thermal energy. The solar heat is not only applied directly to melt the limestone, it also provides heat to assist in the electrolysis of the limestone. In electrolysis, a current applied to the limestone changes the chemical reaction so that instead of separating into lime and CO_2, the limestone separates into lime and some other combination of carbon and oxygen atoms, depending on the temperature of the reaction. When electrolyzed below 800°C, the molten limestone forms lime, C, and O_2. When electrolyzed above 800°C, the product is lime, CO, and $\frac{1}{2}O_2$.

"Electrolysis changes the product of the reaction of the limestone as it is converted to lime," coauthor Stuart Licht, a chemistry professor at George Washington University, told *Phys.org*. "Rather than producing carbon dioxide, it reduces the carbon dioxide (adds electrons) and produces only oxygen and graphite (which can be readily stored as solid carbon) or CO for fuels, plastics or pharmaceuticals. This is accomplished at low energy and high throughput."

When separated, the carbon and oxygen atoms no longer pose the threat to the atmosphere that they do as CO_2. As Licht explained, the carbon monoxide byproduct in the higher temperature reaction can be used in other industries, such as to produce fuels, purify nickel, and form plastics and other hydrocarbons. Plus, the carbon monoxide is produced significantly below market value by this solar thermal electrolytic process. The main product, lime, doesn't react with the other byproducts, but instead forms a slurry at the bottom of the vessel where it can easily be removed.

"This study presents a low-energy, entirely new synthetic route to form CaO without any carbon dioxide emission, and is based on unexpected solubility behavior in molten salts," Licht said. "This synthesis can be accomplished without solar energy, and without our new STEP process, but is particularly attractive when combined with this new solar process. Alternatively, the new synthesis could be used by industry to produce cement using any non-solar renewable or nuclear energy without any CO_2 release, or greatly decrease CO_2 if fossil fuels were used to drive the new cement production (in the latter, worst-case scenario, the products are lime, graphite and oxygen; there is still no CO_2 product, but CO_2 would be used in the energy to drive the process)."

According to the researchers, the STEP process can be performed at a lower projected cost than the existing cement industry process. In fact, when accounting for the value of the carbon monoxide byproduct, the cost of the lime production is actually negative. The researchers' rough analysis shows that the total cost of the limestone material, solar heat, and electricity is \$173 per ton of lime and 0.786 tons of carbon monoxide (0.786 tons of carbon monoxide are produced for every ton of lime). The market value of carbon monoxide is \$600 per ton, or \$471 per 0.786 tons. So after selling the carbon monoxide, the cost of the lime production is \$173 - \$471 = -\$298 per ton. For comparison, the cost to produce lime in the conventional way is about \$70 per ton. The researchers emphasize that this analysis is not comprehensive, but it indicates the cost benefit of STEP cement, not even considering the value of eliminating CO_2 emissions.

The scientists add that the STEP process could be extended beyond cement production to other applications that convert limestone to lime, such as purifying iron and aluminum; producing glass, paper, sugar, and agriculture; cleaning smoke stacks; softening water; and removing phosphates from sewage.

The next challenge for the researchers lies in scaling up the process for commercialization. They note that Gemasolar, a large-scale solar thermal plant, is already in operation. Other solar thermal plants are following, with electricity costs expected to decrease. To maintain constant operation, molten salt storage of the thermal energy can allow production to continue even during fluctuations in sunlight and at night. Another issue may be finding enough lithium carbonate for the electrolyte, although the metal is not consumed in the STEP process and so is not a recurring cost.

"We plan to scale up the outdoor STEP cement prototype, and in general want to increase the portfolio of useful chemicals made by our new solar process," Licht said. "The goals are to replace today's fossil fuel economy with a renewable chemical economy. Scale-up is the challenge. Although the process is entirely new, the individual components (solar towers, 24/7 operation storing solar energy with molten salts) are already in place. Solar energy can be used to efficiently make products without carbon dioxide, and at solar energy efficiencies higher than in photovoltaics."

More information: Stuart Licht, et al. "STEP Cement: Solar Thermal Electrochemical Production of CaO without CO2 emission." *Chem. Commun.*, DOI: **10.1039/C2CC31341C**

DAILY COMMERCIAL NEWS
AND CONSTRUCTION RECORD

June 5, 2012

http://www.dcnonl.com/article/id49775/--a-sprinkle-of-solar-power-in-cement-recipe

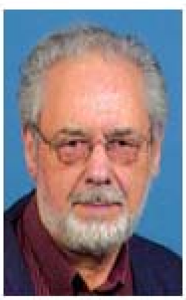
Column | Korky Koroluk

A sprinkle of solar power in cement recipe

A team of scientists at George Washington University, in the United States, has developed a way to use solar energy to produce cement without emitting any carbon dioxide.

It's good news for the construction industry, which has been concerned about carbon dioxide emissions for years.

The present process for manufacturing cement has an immense carbon footprint, around five or six per cent of global greenhouse gas emissions. For every tonne of cement produced, 900 kilograms of carbon dioxide is released into the atmosphere. And the world uses about three billion tonnes of cement every year, releasing 2.7 billion tonnes of carbon dioxide.


Construction Corner
Korky Koroluk

Carbon dioxide is produced in two stages of cement production: the process of decarbonation, in which limestone is separated into lime and carbon dioxide; and burning fossil fuels to heat the limestone to start the decarbonation process.

The new process, dubbed STEP for Solar Thermal Electrochemical Production, eliminates the need for fossil fuel. Instead, concentrated sunlight is used to melt salts in a large storage tank. The hot molten salt is then used not only to melt the limestone, but also to provide heat to assist in the electrolysis of the limestone.

In electrolysis a current is applied to the limestone, changing the chemical reaction so that instead of separating into lime and carbon dioxide, the limestone separates into lime and other combinations of carbon and oxygen atoms, depending on the temperature of the reaction.

By controlling the temperature, the gas byproduct can be carbon monoxide, which is used in some fuels, plastics and pharmaceuticals. Selling it could be profitable enough to more than offset the cost of cement manufacture. The upshot would be cheaper cement with no greenhouse gases.

Stuart Licht, research team leader, says that use of the STEP process could be extended beyond cement production. The team has published a paper showing that a variation of the STEP process can produce pure iron from two common ores—hematite and magnetite, without emitting carbon dioxide. That's important because the iron industry sends 6.8 trillion tonnes of carbon dioxide into the air from its blast furnaces every year.

STEP could also be used for producing glass, paper and sugar, for softening water, and for removing phosphates from sewage.

The next task facing Licht and his team is scaling up the process for commercialization. That shouldn't be too hard because the solar thermal technology is already proven and in use in Spain and parts of the U.S., with more such plants under construction or planned elsewhere.

Ultimately, though, this is about far more than producing cement, or iron, or glass. It's about capturing and sequestering carbon dioxide in the form of solid carbon.

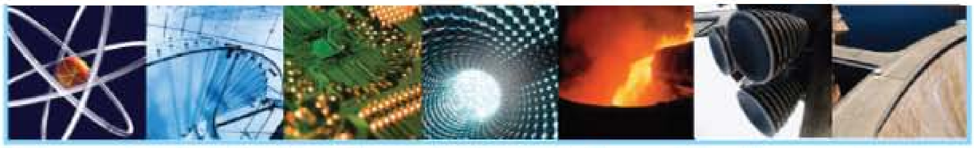
Part of Licht's research is aimed at increasing the "portfolio of useful chemicals made by our new solar process." And that's important because the long-range goal is "to replace today's fossil fuel economy with a renewable chemical economy." To this end, Licht says his team is exploring the STEP generation of synthetic jet fuel and synthetic diesel. That would be done by using carbon monoxide from the STEP process and hydrogen obtained by using STEP to hydrolyze water.

Ellen Stechel, manager of concentrated solar technologies at Sandia National Laboratories in the U.S., says using the sun for manufacturing and for fuel production is an "interesting approach," which she believes can possible. And because of the simplicity of the electrolysis cells Licht uses, she believes the process can be cost-competitive.

That might sound like pie in the sky, but it's an idea the Licht has developed, step by careful step, for a number of years, publishing papers as his work progressed.

And STEP's possibilities are so immense, that scientists worldwide are watching closely.

CERAMIC TECH TODAY



Solar cement — Solar-driven electrolysis for making lime and no CO2 emission

Edited By Eileen De Guire • April 12, 2012

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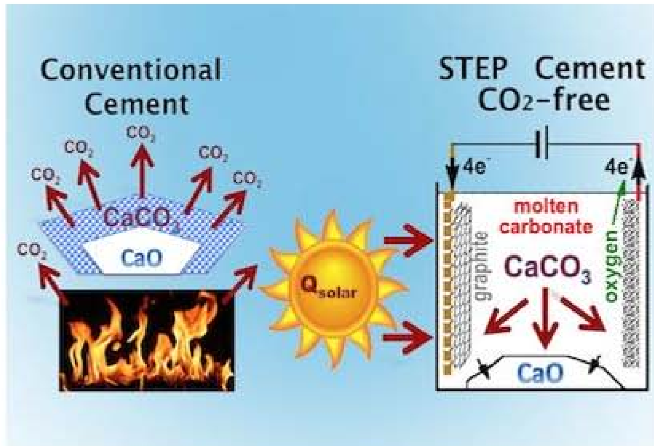


Conventional thermal decomposition of calcium carbonate for cement-making generates almost as much CO_2 as lime. Solar-driven electrolysis of calcium carbonate yields calcium oxide and carbon (or carbon monoxide) and oxygen. Credit: Licht; George Washington University.

Energy gurus often talk about reducing CO_2 emissions. Why not be more aggressive and talk about eliminating CO_2 emissions? And, why not start with a heavy CO_2-producing industry, such as cement?

Some estimate that cement production generates five to six percent of all anthropogenic (human-generated) CO_2 emission. There is an almost one-to-one correspondence of CO_2 generated to cement made — 10 kg of cement generates 9 kg of CO_2. The global annual consumption of cement is more than 3×10^{12} kg , and 90 percent of that is a lot of CO_2. That translates to about 3,300 million tons of cement and just under 3,000 million tons of CO_2.

Indeed, cement researchers often ponder how to to significantly reduce the emissions problem, and many strides have been made in partnership with large cement makers.

The cement-making process generates CO_2 from the decomposition reaction of calcium carbonate to calcium oxide (lime) and from the combustion of fossil fuels to fire kiln reactors (to about 900˚C). Ninety percent or so of the total energy needed to make concrete is used just to make the cement.

Decomposition is a brute force approach to making lime — heat the stuff until it gives up its bonds and falls apart. Professor Stuart Licht at George Washington University is a STEP ahead, though, and has demonstrated the feasibility of making lime by electrolysis with a process he calls Solar Thermal Electrochemical Production. In a paper published this month in *Chemical Communications*, (DOI: 10.1039/C2CC31341C), he describes a solar-driven process that exploits "a new thermal chemistry, based on anomalies in oxide solubilities, to generate CaO, without CO_2 emission."

In the process, molten carbonates heated by solar energy are electrolyzed and form oxides, which in the presence of calcium carbonate precipitate as lime. The solubility of calcium carbonate is high in molten carbonates at high temperatures (in the 750-950˚C range). However, the solubility of calcium oxide in molten carbonates is low, up to 100 times lower than calcium carbonate.

The team experimented with two kinds of electrolyte, a eutectic mix of carbonates and pure lithium carbonate. The paper explains how lime forms in the electrolytic cell, "when molten carbonates undergo electrolysis to form oxides, added calcium carbonate will precipitate the desired CaO product for extraction, and the added carbonate replenishes the electrolyte for continued, ongoing CaO production."

At temperatures below 800˚C, the calcium carbonate electrolyzes to CaO, C and O_2. Above 800˚C, the reaction products are CaO, CO and O_2. (CO is a commercially valuable compound.) No CO_2 is produced in either temperature regime.

Electrolysis of carbonates is endothermic, which means much of the thermal energy required to drive the process can be provided by solar energy. And, if all of the heat is provided by solar energy, no fossil fuels are burned and no CO_2 is generated by the process itself.

The resulting calcium oxide is high density and appears to be easy to harvest as it "forms a slurry at the bottom of the vessel where it may be removed by tap in the same manner in which molten iron is removed from conventional iron production kilns."

The authors realize that scaling-up to industrial production levels and incorporation into production systems will be challenging. But, this is familiar territory for industries and engineers. There is precedent, too, for industrial-scale electrolysis processes. Electrolysis is the basis of the Hall-Heroult process (pdf) for extracting aluminum from bauxite. Similar to Licht's experiment, the key step is to dissolve alumina in a molten salt, in this case, sodium aluminum fluoride.

Is It Possible To Produce Cement Without Releasing High Levels Of Carbon?

News & Events - Engineering News

May 18, 2012

A novel way of making cement could help drastically reduce the greenhouse gas emissions generated during the process, MIT's Technology Review reports.

Producing lime, the most important ingredient in cement mixtures, releases a significant amount of greenhouse gases into the atmosphere every year. Companies that specialize in crafting cement have long struggled to devise more efficient ways of generating lime, but their efforts have often stalled.

Researchers at George Washington University recently unveiled a proof of concept that would allow for the production of lime without many of the deleterious environmental consequences that result from conventional strategies. If the model proves viable, it could help revolutionize the cement industry, experts contend.

Cement production accounts for approximately six percent of all greenhouse gas emissions annually. Generating lime is by far the most carbon-intensive part of the process, according to the news provider. Such is true because of a number of factors, including the fact that firms routinely employ fossil fuels to heat limestone to exceedingly hot temperatures, often in excess of 1,500 degrees Celsius.

Replacing fossil fuels with renewable energy sources is complex, however, and would not necessarily address another intrinsic obstacle: to generate lime from limestone, which is calcium carbonate, it must be heated until carbon dioxide is released. Scientists at GW concentrated their engineering research on tweaking the traditional technique.

Instead of simply implementing solar cells to help power the reactions, the researchers developed a system that converts the resultant carbon dioxide into oxygen and either carbon or carbon monoxide. To achieve such an outcome, they engineered a scheme that employs both electrolysis and heat. What's more, they used a mixture of calcium carbonate and liquid lithium carbonate to increase its effectiveness.

The compound is molten around 900 degrees Celsius, a property that cut the amount of electricity needed in electrolysis, which in turn helps separate lime, according to the scientists. Aside from helping cut carbon emissions, the process also costs less than conventional methods, the researchers noted. PhysOrg reports that by introducing electrolysis into the process, scientists were ultimately able to change the reaction's byproducts.

"Electrolysis changes the product of the reaction of the limestone as it is converted to lime," Stuart Licht, a chemistry professor at GW, said in an interview with Phys Org. "Rather than producing carbon dioxide, it reduces the carbon dioxide [adds electrons] and produces only oxygen and graphite [which can be readily stored as solid carbon] or CO for fuels, plastics or pharmaceuticals. This is accomplished at low energy and high throughput."

Additionally, they contended that it could help significantly reduce projected greenhouse gas levels over the next few decades, especially as developing nations ratchet up their cement production as they undertake massive infrastructure projects.

"Although the process itself is entirely new, the individual components are already in place," said Licht. "Solar energy can be used to efficiently make products without carbon dioxide, and at solar energy efficiencies higher than in photovoltaics."

The researchers recently published their findings in Chemical Communications.

Green Car Congress

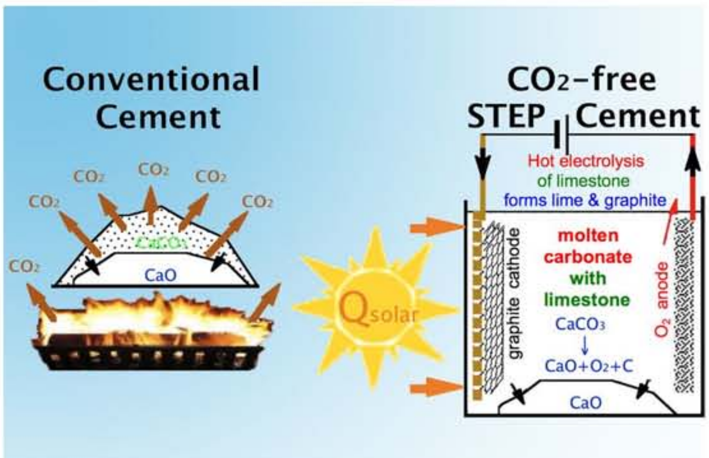
Energy, Technologies, Issues and Policies for Sustainable Mobility

5 June 2012

GWU team develops cost-effective solar process to produce lime for cement without CO2 emission

11 April 2012

http://www.greencarcongress.com/2012/04/licht-20120411.html



Conventional thermal decomposition production of lime (left) versus STEP direct solar conversion of calcium carbonate t calcium oxide (right). Click to enlarge.

A team at George Washington University has demonstrated a new solar process that can produce lime (CaO) for cement without any emission of carbon dioxide, and at lower projected cost than the existing cement industry process. Production of cement accounts for 5-6% of all anthropogenic CO_2 emissions, generating 9 kg of the greenhouse gas for each 10 kg of cement produced, notes Dr. Stuart Licht and his colleagues in a paper on their process accepted for publication in the RSC journal *Chemical Communications*. The majority (about 60%) of those CO_2 emissions result from the production of lime.

The Solar Thermal Electrochemical Production of CaO without CO_2 (STEP Cement) process is based on the STEP theory of an efficient solar chemical process, based on a synergy of solar thermal and endothermic electrolyses, introduced by Licht and his colleagues in 2009. (Earlier post, earlier post.)

> *The majority of CO_2 emissions occurs during the decarbonation of limestone ($CaCO_3$) to lime (CaO)...and the remainder (30 to 40%) from burning fossil fuels, such as coal, to heat the kiln reactors to ~900°C.*
>
> *...Here we show a new thermal chemistry, based on anomalies in oxide solubilites, to generate CaO, without CO2 emission, in a high throughput, cost effective, environment conducive to the formation of cement. The aqueous solubility of $CaCO_3$ ($6x10^{-5}$ m, where molal ≡ moles per kg solvent) is 3 orders of magnitude less than the $2x10^{-2}$ m solubility of calcium oxide, dissolving as calcium hydroxide. Surprisingly, this situation is reversed at high temperatures in molten carbonates, which allows the endothermic, electrolytic one pot synthesis, and precipitation of CaO. Conducive to our new solar process, electrolysis of molten carbonates forms oxides, which precipitate as calcium oxide when mixed with calcium carbonate. Thus no CO_2 is formed, to eliminate cement's greenhouse gas contribution to anthropogenic climate change.*
>
> —Licht *et al.*

STEP Cement uses solar thermal energy to drive calcium oxide production without any emission of CO_2 in a one pot synthesis; solar thermal energy is used both for the enthalpy of calcium oxide formation from calcium carbonate and to decrease the required electrolysis potential.

In the process, limestone undergoes low energy electrolysis to produce (i) CaO; (ii) O_2 and (iii) reduced carbonate without carbon dioxide emission.

Molten carbonate electrolytic synthesis operates in the reverse mode of molten carbonate fuel cells (MCFC); rather than injecting fuel to produce electricity as a product as in the MCFC, electrical energy is supplied and energetic chemical products are generated. Carbonate electrolysis is endothermic, which provides the opportunity to add a significant portion of the required energy to drive the process as solar thermal heat. When the requisite low energy of the solar-heated electrolysis is generated by a non-fossil fuel electricity source, the process is fully carbon dioxide free.

In their STEP electrolysis experiments, Licht *et al.* used three electrolyses in series, with lithium carbonate using thin planar nickel and steel electrodes, as detailed in the Electronic Supplementary Material (ESI) for the paper.

The STEP Cement process, the authors note, also cogenerates a more valuable product than cement: either CO or carbon. The CO is produced at below current market values; the low cost of the cogenerated product is due to the endothermic, reactive nature of the available hot carbonate from the limestone, which as they demonstrated in the study, is easily reduced at high activity/low energy in the molten state to carbon or carbon monoxide. CO is an energetic industrial reagent used to produce fuels, purify nickel, and to form plastics and other hydrocarbons.

As a result, the authors suggest, STEP Cement can produce lime at less cost than that of conventional industry cement processes; the projected cost of the produced calcium oxide is decreased by the value of the byproduct, either solid carbon or CO.

> *This study presents a new chemistry of energy efficient, CO_2-free lime production, and the challenge of system engineering and scale-up awaits. It should be noted that the carbonate product is readily removed (dropping cleanly from the extracted steel wire cathode when it is uncoiled, or at higher temperature as a simple evolved gas (CO)), oxygen evolution is confined to the vicinity of the anode, and the high density calcium oxide product is not reactive (does not decompose) in the molten carbonate and forms a slurry at the bottom of the vessel where it may be removed by tap in the same manner in which molten iron is removed from conventional iron production kilns.*
>
> —Licht *et al.*

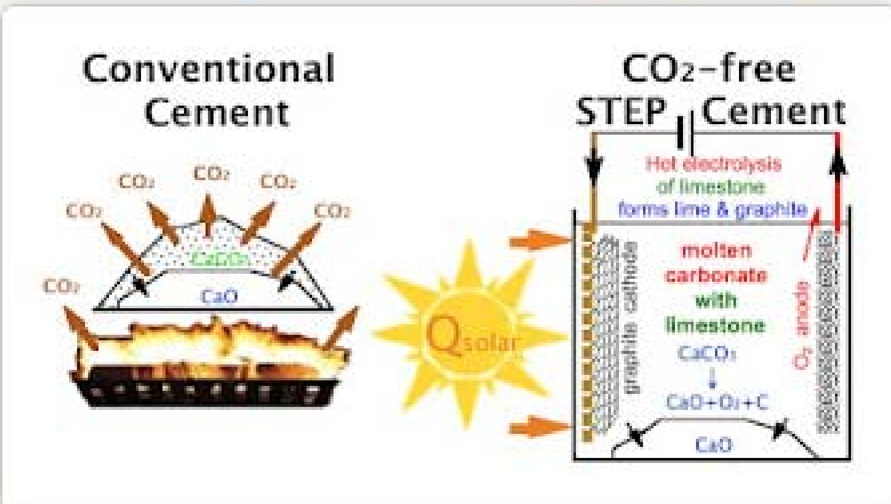
Resources

- Stuart Licht, Hongjun Wu, Chaminda Hettige, Baohui Wang, Joseph Asercion, Jason Lau and Jessica Stuart (2012) STEP Cement: Solar Thermal Electrochemical Production of CaO without CO_2 emission. *Chem. Commun.*, 2012, Accepted Manuscript doi: 10.1039/C2CC31341C
- Electronic Supplementary Material

Linguaggio Macchina

09 aprile 2012

Come produrre cemento "Carbon Free" grazie al Sole. Una ricerca della George Washington University di Ashburn (Virginia)



Attualmente per ogni 10 kg di cemento prodotto vengono rilasciati 9 kg di anidride carbonica. In un articolo pubblicato il 5 aprile 2012 su rivista Chemical Communication, Stuart Licht e altri sei ricercatori della George Washington University di Ashburn (Virginia, USA) illustrano il loro metodo di produzione di cemento da fonte solare.

STEP Cement: Solar Thermal Electrochemical Production of CaO without CO2 emission

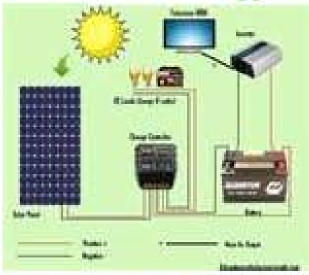
Stuart Licht, Hongjun Wu, Chaminda Hettige, Baohui Wang, Joseph Asercion, Jason Lau, Jessica Stuart

Abstract

New molten salt chemistry allows solar thermal energy to drive calcium oxide production without any carbon dioxide emission. This is accomplished in a one pot synthesis, and at lower projected cost than the existing cement industry process, which after power production, is the largest contributor to anthropogenic greenhouse gas emissions.

The Licht research group has taken on the challenge of a comprehensive solution to climate change. We're working towards changing today's fossil fuel, to a renewable chemical economy, replacing the largest greenhouse gas emitters, including iron & fuel production, by new, inexpensive, solar, CO2-free, chemistries.

New Cement-Making Method Could Slash Carbon Emissions – Technology Review



May 12, 2012

Researchers at George Washington University have bolted together an ungainly contraption that they say efficiently uses the energy in sunlight to power a novel chemical process to make lime, the key ingredient in cement, without emitting carbon dioxide. the device puts to work about half of the energy in sunlight (solar panels, in comparison, convert just 15 percent of the energy in sunlight into electricity).

Cement production alone emits 5 to 6 percent of total man-made greenhouse gases, and most of that comes from producing lime. Some of the greenhouse-gas emissions from conventional cement production come from using fossil fuels to heat up limestone to high temperatures—about 1,500 ^{0}C. Replacing fossil fuels with renewable energy is straightforward, but not necessarily economical. the new work focuses on a harder problem. about 60 percent of the carbon-dioxide emissions from cement production is inherent to the process. Lime is made by heating up limestone—that is, calcium carbonate—until it releases carbon dioxide.

The new process changes the chemistry. Rather than emitting carbon dioxide, it converts the gas, using a combination of heat and electrolysis to produce oxygen and either carbon or carbon monoxide, depending on the temperatures employed. both carbon and carbon monoxide are useful products that might otherwise have been made using fossil fuels.

To make the electrolysis practical, the researchers mixed solid calcium carbonate with liquid lithium carbonate, which is molten at the temperatures that are optimal for the process—about 900 ^{0}C. the liquid form is conducive to electrolysis. the elevated temperatures lower the amount of electricity needed to electrolyze, and cause the lime to precipitate out of the mixture, making it easy to collect. (At lower temperatures, the lime is more soluble, so it doesn't precipitate.)

To demonstrate the process, the researchers built a device that includes three Fresnel lenses for concentrating sunlight. two of those heat up the mixture of lithium carbonate and limestone. Those are the largest lenses. Their relative size reflects the fact that most of the energy needed for the process goes to heating up the mixture. the third, smaller lens focuses light on a high-efficiency solar cell, which provides the relatively small amount of electricity needed to electrolyze the hot carbonate mixture.

The device is just a proof of concept, not ready for commercialization. It's small, and it works only when it's sunny—and intermittent operation isn't ideal for an industrial process. the researchers propose using molten salt to store heat, a system used in some solar thermal power plants. that would allow the process to run day and night. the electricity could come from using the heat to generate steam to spin a turbine, as in a solar thermal power plant, or from any other source of electricity.

Stuart Licht, the professor of chemistry at George Washington University who led the work, estimates that the process, if it can be scaled up, could be cheaper than conventional lime production. He says it's more efficient than solar panels because it uses parts of the solar spectrum that solar cells can't efficiently convert into electricity.

The process still requires a lot of energy, says C12 Energy CEO Kurt House, who has developed low-carbon concrete production processes. "It comes down to how you want to use solar energy," he says. "If the efficiency is as good as they say it is, then I agree, this is very, very interesting. but I'm skeptical."

treehugger
A DISCOVERY COMPANY
April 25, 2012

Solar Powered Process Could Finally Make Concrete Greener

Concrete is among the most common building materials in the world, and it has a massive carbon footprint. The 15% of concrete that is cement is behind five to six percent of all man made CO_2, producing nine kilograms of carbon dioxide for every ten kilograms of cement. A new solar process may put a big dent in those numbers.

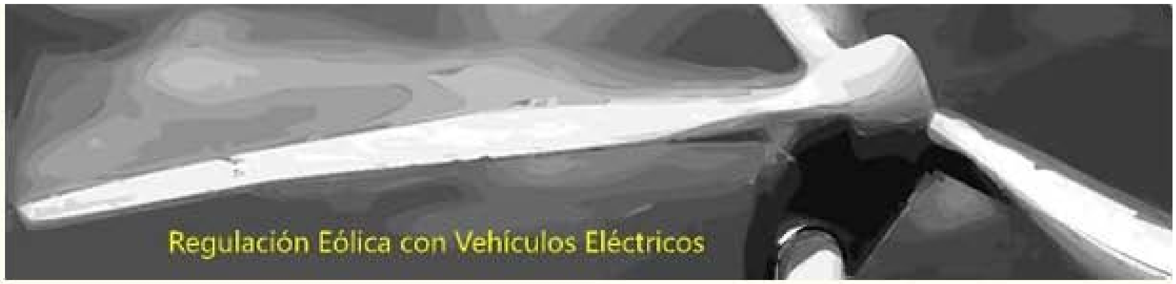
Researchers at The George Washington University have developed a process called Solar Thermal Electrochemical Production (STEP) of CaO without CO_2, reported Green Car Congress. As the name implies, it's a way to produce the lime that goes into cement without yielding CO_2.

As Lloyd noted a few years ago: "The chemical reaction that creates cement releases large amounts of CO_2 in and of itself. Sixty percent of emissions caused by making cement are from this chemical process alone."

The GWU team, led by Dr. Stuart Licht, goes after that chemical reaction and that 60 percent:

> The majority of CO_2 emissions occurs during the decarbonation of limestone ($CaCO_3$) to lime (CaO)...and the remainder (30 to 40%) from burning fossil fuels, such as coal, to heat the kiln reactors to ~900°C.

The "new thermal chemistry" relies on "anomalies in oxide solubilites" to cut out the production of CO_2 in the making of cement. It remains to be seen how STEP can be translated to the industrial model, if it will be practical and cost-effective. If all goes well, concrete could bump off bamboo as the new green building material du jour.



Cement Production with Concentrated Solar Thermal Power

april 12, 2012

Concentrating Solar Power would be used. And not just to heat the limestone – but also to help in electrolysis. This would produce a different chemical reaction without a carbon dioxide byproduct.

In a study published in a recent issue of Chemical Communications, a team of researchers from Virginia's George Washington University explain a revolutionary way to make lime cement that releases zero CO_2 emissions – and costs less too.

After coal-powered electricity, cement manufacture is the next biggest emitter of greenhouse gases, because cement is ubiquitous in modern life.

It is needed for virtually all skyscrapers, bridges and freeway overpasses and many other buildings and structures including nuclear power plants. The world consumes about 3 trillion kg of cement annually.

Pound for pound, kilogram for kilogram, ton for ton, every 10 units of cement will release 9 units of CO_2. So it is a huge problem for the increasingly unstable climate we are creating for ourselves.

Of the two ways that making cement releases carbon dioxide, separating the lime from the limestone (decarbonation, or removing the carbon atom and two oxygen atoms in limestone ($CaCO_3$) to obtain lime (CaO) with CO_2) accounts for 70% of the emissions.

The other 30% is because it takes a lot of heat to heat the kiln reactors, burning fossil fuels.

Solar thermal power would be used. And not just to heat the limestone – but also to help in electrolysis. This would produce a different chemical reaction without a carbon dioxide byproduct.

In electrolysis, a current applied to the limestone changes the chemical reaction so that instead of separating into lime and CO_2, the limestone separates into lime and some other combination of carbon and oxygen atoms, depending on the temperature of the reaction.

When electrolyzed below 800°C, the molten limestone forms lime, C, and O_2. When electrolyzed above 800°C, the product is lime, CO, and $\frac{1}{2}O_2$.

Instead of a CO_2 byproduct, their reactions produce useful industrial chemicals. Their carbon monoxide byproduct (in the higher temperature reaction) can be used to make fuels, purify nickel, and form plastics and other hydrocarbons.

This makes it cheaper than current lime production which costs $70 a ton, because the CO can be sold.

The researchers' rough analysis shows that the total cost of the limestone material, solar heat and electricity is $173 per ton of lime and 0.786 tons of carbon monoxide (0.786 tons of carbon monoxide are produced for every ton of lime).

The market value of carbon monoxide is $600 per ton, or $471 per 0.786 tons. So after selling the carbon monoxide, the cost of the lime production is actually a negative number. $173 – $471 = minus $298 per ton.

No carbon emissions. Cheap. And even better, it has wide applications.

Nearly all of the other heaviest emitters could similarly be stripped of their greenhouse gas problem with this technology, the scientists say.

(Among other industries, these industrial processes include purifying iron and aluminum, making glass, paper, sugar, and agriculture, cleaning smoke stacks, softening water, and removing phosphates from sewage.)

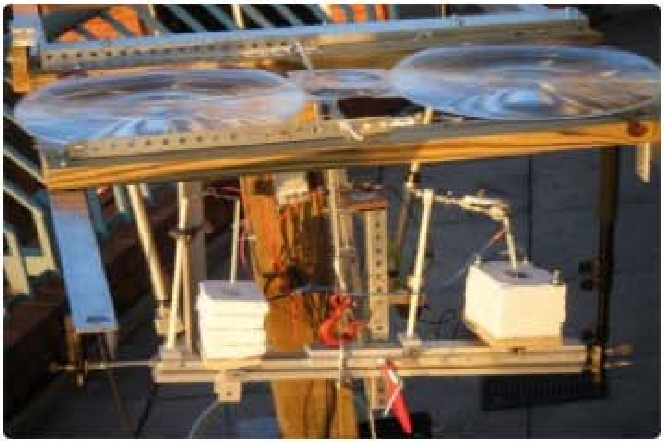
The next step would be is simply scaling up the fairly straightforward process for commercialization. "Although the process itself is entirely new" coauthor Stuart Licht, a chemistry professor at George Washington University, told Phys.org."the individual components (solar towers, 24/7 operation storing solar energy with molten salts) are already in place. Solar energy can be used to efficiently make products without carbon dioxide, and at solar energy efficiencies higher than in photovoltaics."

The timing is perfect: a burgeoning Asia is about to build the new mega cities of the 21st century. And super hot solar thermal heat is ready: Halotechnics Molten Glass Thermal Storage Could Mean 6 Cent Solar.

In the electrolysis process alone, even without solar power, but using fossil heat source, "worst case scenario" says Licht, "the products are lime, graphite and oxygen; there is still no CO_2 product, but CO_2 would be used in the energy to drive the process."

Stuart Licht, et al. "STEP Cement: Solar Thermal Electrochemical Production of CaO without CO2 emission." Chem. Commun., DOI: 10.1039/C2CC31341C

Solar Powered Cement Production Technology Takes Off at George Washington University



By Ovidiu Sandru on May 18, 2012

The Green Optimistic
alternative energy news, environmental awareness

Right now, cement production accounts for 5 to 6 percent of total man-made greenhouse gases. Producing lime, its key ingredient, uses an energy-intensive process that needs temperatures as high as 1,500 degrees Celsius, and that can only be obtained with fossil fuels. A new, rudimentary contraption at George Washington University does all that with solar power and without emitting carbon dioxide.

The team led by **Stuart Licht** used three Fresnel lenses to concentrate sunlight onto two different processes: one that heats up limestone and the other that produces electricity to perform electrolysis, that breaks the hot carbonate mixture and causes the lime to precipitate out of it, making it readily-collectible.

Around 60 percent of the carbon dioxide emissions from the production of cement is considered to be unavoidable. Licht's team proved otherwise: they "hacked" the process to produce oxygen and carbon/carbon monoxide, which can be further recycled.

By mixing solid calcium carbonate with liquid lithium carbonate, and preheating the solution to 900 degrees Celsius, the scientists make up a liquid that acts like an electrolyte. The high temperature helps the entire electrolysis process to produce lime, which would be harder to collect at lower temperatures, because it would be more soluble.

However, the lime production system has to go a long way until it's commercially-available. One of the roadblocks is that the energy (heat) has to be stored to counter the effects of the intermittent nature of solar power. Cited solutions include storing it in molten salts, just like it's done in CSP (concentrated solar power) systems.

If it proves to work as advertised, this technology could offset up to 6 percent of our total greenhouse gas emissions, as I said earlier. What strikes me is that nobody had thought so far about making this contraption possible, and everyone is using expensive fossil fuels, when the Sun is readily available for anyone to use… weird or what?

On the other hand, it's not uncommon for such inventions to create spin-offs that would later become industry leaders. We shall wait and see.

http://www.greenoptimistic.com/2012/05/18/solar-powered-cement-production/

DISCOVER®
MAGAZINE

Technology / Alternative Energy

Turning Carbon Dioxide Into Bioplastics: 2 Birds With 1 Stone?

One chemist says he can slash atmospheric carbon dioxide to preindustrial levels in a decade, harnessing the sun's power to make useful products at the same time.

by Elizabeth Svoboda
published online August 1, 2011

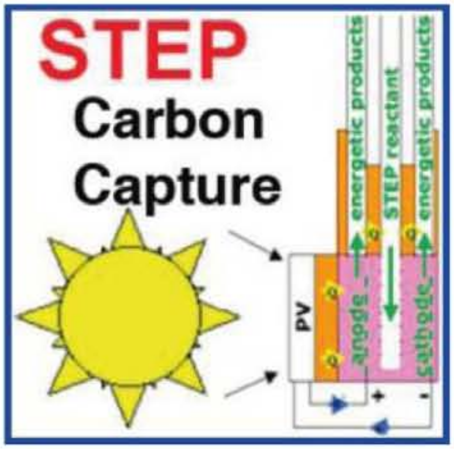
Stuart Licht's STEP (Solar Thermal Electrochemical Production) process uses solar energy to break down atmospheric CO_2 and other compounds into their constituent elements. These elements would ultimately be recombined to make plastics and fuel.

At the heart of the STEP (pdf) process is an electrolysis cell, a device that uses electricity to break down chemical compounds. A prototype version of the cell, consists of two electrodes—positively and negatively charged—submerged in a chemical bath containing the target compound. When electric current passes through the cell, positively charged ions from the compound are attracted to the negative coil and negatively charged ions are attracted to the positive coil, splitting the material and yielding its constituent elements along with new compounds.

The hotter the contents of the cell, the less voltage required to initiate this reaction. Using heat from an external solar array, Licht, who's based at George Washington University, can raise the temperature so high that only a minute electrical current, supplied by solar photovoltaic cells, is needed to split the compounds. When carbon dioxide is fed into the cell, electricity splits it into oxygen and solid carbon or carbon monoxide gas that could then be used to manufacture many different products and fuels.

Scientists have been watching Licht's progress closely. "It's an interesting approach to using the sun for manufacturing and fuel production," says Ellen Stechel, manager of concentrated solar technologies at Sandia National Laboratories. "But can it be cost-competitive?" Because of the cell's simplicity, Licht says, the answer is yes. If he could construct STEP solar arrays dispersed across 4 percent of the Sahara, he would be able to convert 92 billion tons of carbon dioxide into solid carbon each year. At that rate, he could eliminate one-tenth of all the carbon dioxide released since the Industrial Revolution in a single year.

Solar-powered process could decrease carbon dioxide to pre-industrial levels in 10 years



In the Solar Thermal Electrochemical Photo (STEP) carbon capture process, the sun's visible light and heat are used to capture large amounts of carbon dioxide from the atmosphere and convert it to solid carbon for storage or carbon monoxide for fuel generation. Image copyright: Stuart Licht, et al. ©2010 American Chemical Society.

(PhysOrg.com) -- By using the sun's visible light and heat to power an electrolysis cell that captures and converts carbon dioxide from the air, a new technique could impressively clean the atmosphere and produce fuel feedstock at the same time. The key advantage of the new solar carbon capture process is that it simultaneously uses the solar visible and solar thermal components, whereas the latter is usually regarded as detrimental due to the degradation that heat causes to photovoltaic materials. However, the new method uses the sun's heat to convert more solar energy into carbon than either photovoltaic or solar thermal processes alone.

The new process, called Solar Thermal Electrochemical Photo (STEP) carbon capture, was recently suggested theoretically by a team of scientists from George Washington University and Howard University, both in Washington, DC. Now, in a paper just published in *The Journal of Physical Chemistry Letters*, the scientists have experimentally demonstrated the STEP process for the first time.

"The significance of the study is twofold," Stuart Licht, a chemistry professor at George Washington University, told *PhysOrg.com*. "Carbon dioxide, a non-reactive and normally difficult-to-remove compound, can be easily captured with solar energy using our new low-energy, lithium carbonate electrolysis STEP process, and with scale-up, sufficient resources exist for STEP to decrease carbon dioxide levels in the atmosphere to pre-industrial levels within 10 years."

As the scientists explain, the process uses visible sunlight to power an electrolysis cell for splitting carbon dioxide, and also uses solar thermal energy to heat the cell in order to decrease the energy required for this conversion process. The electrolysis cell splits carbon dioxide into either solid carbon (when the reaction occurs at temperatures between 750°C and 850°C) or carbon monoxide (when the reaction occurs at temperatures above 950°C). These kinds of temperatures are much higher than those typically used for carbon-splitting electrolysis reactions (e.g., 25°C), but the advantage of reactions at higher temperatures is that they require less energy to power the reaction than at lower temperatures.

The STEP process is the first and only method that incorporates both visible and thermal energy from the sun for carbon capture. Radiation from the full solar spectrum - including heat - is not usually considered an advantage in solar technologies due to heat's damage to photovoltaics. Even in the best solar cells, a large part of sunlight is discarded as intrinsically insufficient to drive solar cells as it is sub-bandgap, and so it is lost as waste heat.

By showing how to take advantage of both the sun's heat and light for capturing and splitting carbon dioxide, the STEP process is fundamentally capable of converting more solar energy than either photovoltaic or solar thermal processes alone. The experiments in this study showed that the technique could capture carbon dioxide and convert it into carbon with a solar efficiency from 34% to 50%, depending on the thermal component. While carbon could be stored, the production of carbon monoxide could later be used to synthesize jet, kerosene, and diesel fuels, with the help of hydrogen generated by STEP water splitting.

"We are exploring the STEP generation of synthetic jet fuel and synthetic diesel," Licht said, "and in addition to carbon capture, we are developing STEP processes to generate the staples predicted in our original theory, such as a variety of metals and bleach."

More information: Stuart Licht, Baohui Wang, Susanta Ghosh, Hina Ayub, Dianlu Jiang, and Jason Ganley." *J. Phys. Chem. Lett.* 2010. 11 2363-2368. DOI:10.1021/jz100829s

STEP:

A different solar energy conversion process

Solar Thermal Electrochemical Photo generation of energetic molecules

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SCIENCE & TECHNOLOGY CONCENTRATES

AUGUST 2, 2010 | VOLUME 88, NUMBER 31 | P. 37 | DOI: 10.1021/CEN072210105324

Solar Photo-Thermal Electrochemistry Demonstrated

A new process uses the full power of the sun--both visible light and thermal heating--to drive electrochemical reactions

Stephen K. Ritter

A new type of solar-energy process that can use the full power of the sun—both visible light and thermal heating—to drive electrochemical reactions is being reported by **Stuart Licht** of George Washington University and colleagues (*J. Phys. Chem. Lett.*, DOI: **10.1021/jz100829s**). Last year, Licht presented the theoretical basis for the solar thermal electrochemical photo process and proposed that it could be a means for mitigating carbon dioxide emissions (***J. Phys. Chem. C* 2009, *113*, 16283**). Licht and coworkers have now partially demonstrated the concept by using full-solar-spectrum artificial light in combination with a molten lithium carbonate electrolysis cell. CO_2 bubbled into the carbonate reduces to solid carbon on the cell's electrode. Visible light powers a photovoltaic device that drives the electrochemical reduction of CO_2 as the thermal energy heats the system up to as much as 950 °C. The high temperature keeps the carbonate molten and reduces the energy required for the electrolysis. Overall, the system is more energy efficient than photovoltaics or solar thermal processes alone, Licht notes. The solid carbon could be stored or used as a filler material, he says. By adjusting the reaction conditions, CO_2 is reduced to CO, Licht adds, which subsequently could be combined with H_2 to make transportation fuels and chemical feedstocks.

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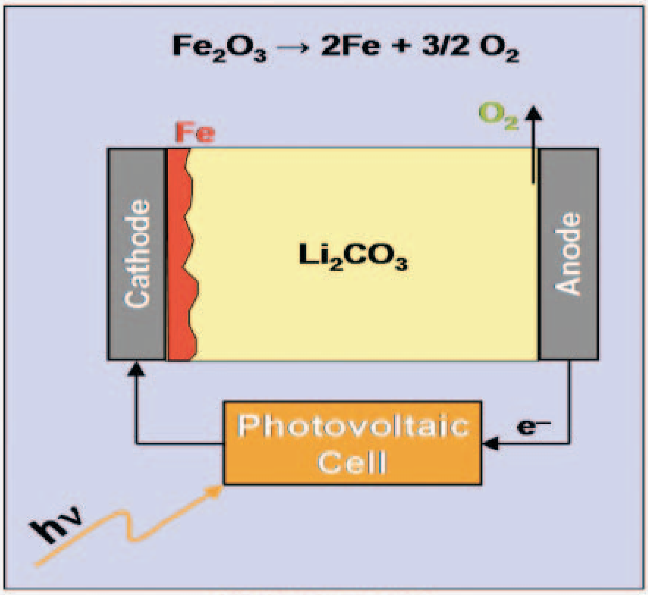
Topics Covered

solar reactor, carbon dioxide, electrolysis, carbon capture

Chemical & Engineering News
ISSN 0009-2347

The Iron Age Reinvented?



STEP production of Fe(0)

First was chemistry, then came writing. Illiterate by definition, prehistoric people had nevertheless been producing their bronze and iron tools for several centuries before they figured out that writing too was an important step forward for humanity. Extraction of iron was carried out by heating its ores (magnetite, Fe_3O_4, and hematite, Fe_2O_3) over a charcoal fire. Carbon reduces Fe(II) and Fe(III) by combining with oxygen to release CO_2; this forms an Fe(0) rich solid. Since then, we replaced charcoal with carbon coke but we essentially produce steel and cast iron in the same way.

As the metallurgic industry is one of the main sources of atmospheric CO_2, a novel technological approach would be a most needed breakthrough.

Research in this direction has taken Prof. Licht at George Washington University (USA) to develop a solar thermal electrochemical photo (STEP) process, as it has been called, that drives iron deposition at the cathode of an electrolytic cell in which the iron ore is dissolved in molten Li_2CO_3 (m.p. 723 °C) heated at 800°C.

Visible light is used to power a photovoltaic cell whose circuit is closed by the electrolysis of the Fe ore. In a testing device, 800 mg of Fe were collected at the cathode following a 0.5-A 6-e^- electrolysis of Fe_2O_3 for 2 hours. If the scaling-up does not present major hurdles, STEP process, could potentially reinvent the way we have been producing iron-based tools for the last 5000 years or so.

["High Solubility Pathway for the Carbon Dioxide Free Production of Iron", S. Licht, B. Wang, *Chem. Commun.* **2010**, 46, 7004.]

Departmental page of Prof. Stuart Licht at George Washington University (USA)

Papers of the same authors on related topics

"A New Solar Carbon Capture Process: Solar Thermal Electrochemical Photo (STEP) Carbon Capture", S. Licht, B. Wang, S. Ghosh, H. Ayub, D. Jiang, J. Ganley, *J. Phys. Chem. Lett*. **2010**, 1, 2363.

"STEP (Solar Thermal Electrochemical Photo) Generation of Energetic Molecules: A Solar Chemical Process to End Anthropogenic Global Warming", S. Licht, *J. Phys. Chem. C* **2009**, 113, 16283.

Sept. 23, 2010
http://beautifulphotochemistry.wordpress.com/2010/09/23/the-iron-age-reinvented/#more-1586

PHOTONICS spectra

October / 2010
page 33
Online at: http://www.photonics.com/Article.aspx?AID=44538

Erasing carbon's footprint with sunshine

Hank Hogan, Contributing Editor, hank.hogan@photonics.com

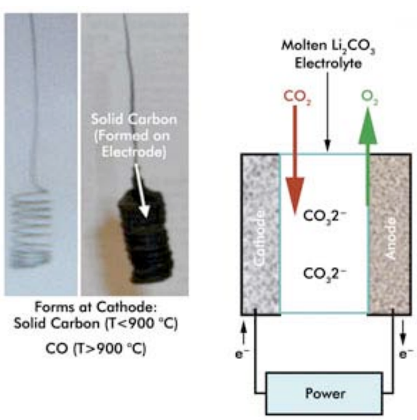
The key to rolling back climate change could be the sun, according to George Washington University researchers who have demonstrated a carbon capture process that promises to use solar power to remove carbon dioxide from the air. As a bonus, the technique could generate a profitable product.

"Because the process simultaneously uses both solar thermal and solar visible, it captures and uses more solar energy than solar cells, and it removes and converts carbon dioxide into a useful form," said Stuart Licht, a chemistry professor at the university's Columbian College of Arts and Sciences in Ashburn, Va.

Licht was lead author on a *Journal of Physical Chemistry Letters* paper published online on Aug. 18, 2009, describing the process, which the researchers dubbed solar thermal electrochemical photo, or STEP, carbon capture. It has a carbon dioxide capture efficiency of up to 50 percent; i.e., as much as half of the energy in sunlight can be used to remove CO_2 from the air.

The end product is solid carbon or carbon monoxide. The latter could be used as feedstock for synthetic jet, kerosene and diesel fuels as well as for plastics and medicine. The revenue derived from selling such feedstock or the solid carbon could change the economics of combating rising CO_2 levels, making mitigation much more attractive.

In a demonstration of the new carbon capture technique, the investigators bubbled CO_2 through an electrolysis cell filled with molten lithium carbonate. They used concentrated solar thermal, or infrared, energy to heat the cell to a temperature above the 723 °C melting point of the material, forcing the temperature as high as 950 °C. They used photovoltaics to convert the visible part of sunlight into electricity that drove the electrochemical reaction.



Sunshine powers an electrolysis cell (right) that turns atmospheric CO_2 into solid carbon (left) or carbon monoxide. Courtesy of Stuart Licht, George Washington University. Reprinted from the Journal of Physical Chemistry Letters.

The high temperature decreased the energy required for that reaction. What's more, the output of that reaction depended upon the temperature.

In their demonstration, the researchers plated out solid carbon on the cathode of the electrolysis cell at temperatures as low as 750 °C. At higher temperatures, the amount of solid carbon decreased and the production of gaseous carbon monoxide increased. At 950 °C, only the gas was produced.

Because the technique is highly immune to poisoning effects, it could be used to directly treat the waste stream coming out of a smokestack, something that Licht noted was not possible with other proposed carbon capture methods.

Calculations showed that it is feasible with STEP carbon capture to reduce CO_2 in the atmosphere to preindustrial levels within 10 years. There is enough annual lithium carbonate production to do this, although it would require a significant fraction of the world's output. Roughly 700 km^2 of photovoltaics would be needed. How long it would take to remove the CO_2, Licht said, depends on the commitment to capturing carbon.

The technique also could use potassium carbonate, of which there is a much larger potential supply than there is of lithium carbonate. The downside is that using potassium would require higher electrolysis potentials and would therefore be not as attractive as the lithium alternative.

The STEP method also could reduce atmospheric CO_2 in other ways. Licht and his team showed in a *Chemical Communications* paper published online on Aug. 23, 2010, that a variation of the STEP technique can produce pure iron from two common ores, hematite and magnetite, without emitting carbon dioxide. This approach could significantly reduce the estimated 6.8 trillion tons of CO_2 emitted each year by the iron industry.

Licht said that the group welcomes commercial or governmental inquiries about the STEP technique. He added that the method can be used for environmentally benign generation of fuels, a process that requires teaming it up with solar-energy-produced hydrogen.

Noting that the extraction of CO_2 from the air is the culmination of efforts stretching over 20 years, he said, "Until now, it has been a challenge to convert the stable molecule carbon dioxide into a useful product and remove it from the atmosphere. It is exciting to watch carbon dioxide be bubbled into the STEP process and be easily converted into solid carbon.

examiner.com
WASHINGTON DC

Using solar energy to power the hydrogen economy of the future

June 6, 6:43 PM Varun Saxena

Hydrogen has the potential to solve the world's energy crisis. It is energetic and abundant, and hydrogen fuel does not emit Carbon Dioxide. Technical and economic challenges have prevented hydrogen from becoming a major source of the world's energy in spite of its promising qualities. But that could change soon. Chemistry Professor Stuart Licht, of George Washington University, and his research team are attempting to perfect a promising method of hydrogen energy production: the solar thermal electrochemical photo conversion of energy, or STEP process, for short. He presented his research at George Washington's annual Solar Symposium, held on April 19th, 2010.

Why is hydrogen fuel the best choice for meeting our transportation demands?
If produced in a sustainable manner, hydrogen fuel is superior to its competitors. Electric cars are constrained by the limitations of the battery and six percent of the energy that is produced is lost on the electrical power grid, according to Licht. Biofuels are an inefficient form of energy production. Their solar to fuel energy efficiencies are less than ten percent. Because of the limitations of photosynthesis, the crops contain about ten percent of the energy that they absorb from the sun, and even more energy is lost during the production of biofuels. In addition, growing feedstock for biofuels pits fuel production against food production, and results in the loss of wilderness.

Why is the STEP process better than other methods of producing hydrogen fuel?
Ninety percent of the hydrogen that is produced is derived from fossil fuels, which results in carbon dioxide emissions. Using solar power to produce hydrogen results in no carbon dioxide emissions. The two methods of producing hydrogen fuel with solar power are the solar thermal method and the solar photovoltaic method. The former method involves heating water up to very high temperatures until it breaks down into its component elements, hydrogen and oxygen. It is technically challenging because the elements tend to recombine when they are brought down to lower temperatures. Many reactions must be performed in order to separate hydrogen from oxygen so that they do not recombine. As a result, over 90% of the initial energy input is lost. Similarly, the solar photovoltaic method is only 10 to 20% solar to hydrogen fuel efficient. It involves using a traditional solar photovoltaic cell to produce electricity, which then splits water. The STEP process can separate hydrogen from water at efficiencies above 30%.

How does the STEP process work?
Unlike the competing methods, the STEP process uses the entire solar spectrum. Dialetic beam splitters, described by Licht as “hot mirrors,” split solar energy into two components, the visible spectrum (employed by the solar photovoltaic method) and the invisible, or thermal spectrum (which is employed by the solar thermal method). The thermal energy is used to heat an electrolysis chamber to molten temperatures, and the visible portion is used to produce electricity to split the water. When the electrolysis chamber is heated, the amount of energy needed to split water falls from 1.2 to .7 volts. Silicon based solar concentrators can generate .8 volts of electricity, enough to split the water at high temperatures.

Because it is a relatively efficient process, and requires a lower voltage to split hydrogen, the STEP process is more cost competitive than competing methods of hydrogen production. According to Licht, independent studies confirm that the STEP process can produce hydrogen at less than half the cost of competing water splitting technologies. As a result, Licht’s research team and partner company Lynntech have signed a contract to built STEP hydrogen generators for the US Air Force. “We can envision someday, a solar hydrogen process in which we might have STEP hydrogen generators generating hydrogen for cars,” Licht proclaimed.

Can the STEP process “split” other molecules?
Yes. The STEP process can be used to create carbon monoxide (CO) from carbon dioxide (C02). The energy needed to split carbon dioxide falls faster than that of water at increasing temperatures, and the result is that carbon monoxide can be created at efficiencies of over fifty percent using the STEP process. Carbon monoxide and hydrogen can be used to make synthetic diesel, and at a lower cost than conventional diesel. Currently synthetic diesel is produced in South Africa. But when coal is converted to carbon monoxide, carbon dioxide is a byproduct. Because the STEP process uses only solar energy, and pure carbon dioxide is used as the input, it can produce synthetic diesel without increasing green house gas emissions.

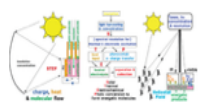
Green Car Congress

Energy, technologies, issues and policies for sustainable mobility

GWU Researcher Developing Efficient Solar Chemical Process for Generation of Energetic Molecules and Conversion of CO2

5 September 2009

Dr. Stuart Licht (earlier post) at George Washington University is developing a solar-driven process that, he says, could efficiently replace current industrial processes for the production of certain energetic molecules such as hydrogen, metals and chlorine, which are responsible for a large component of anthropogenic CO_2. It can also convert captured anthropogenic CO_2, generated by burning fossil fuels, to CO and O_2 via high-temperature electrolysis. A paper on his work is in press for the ACS' *Journal of Physical Chemistry, C*.



(Left) Charge and heat flow in the STEP system. Colored arrows indicate the direction of heat flow (yellow arrows), electron flow (blue), and reagent flow (green). (Right) Auxiliary components to reach higher STEP temperatures and/or decrease the heat incident on the PV. Light harvesting can use various optical concentrators and beam splitters can redirect sub-bandgap radiation away from the PV onto the electrolyzer. Licht, 2009. Click to enlarge.

One third of the global industrial sector's annual emission of $1x10^{10}$ metric tons of CO_2 is released in the production of metals and chlorine. This, together with the additional CO_2 from electrical generation, heating and transportation, comprise the majority of CO_2 emissions.

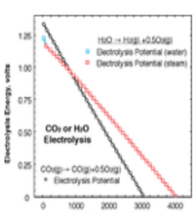
The STEP (Solar Thermal Electrochemical Photo) process fundamentally captures sunlight more efficiently than photovoltaics by using the full (UV, visible and infrared) sunlight. More than 50% of solar energy is captured and used. Conventional photovoltaics lose much of the visible sunlight, and can not use the infrared sunlight at all.

STEP distinguishes radiation that is intrinsically energy sufficient to drive photovoltaic charge transfer and applies all excess solar thermal energy to heat the electrolysis reaction chamber and to decrease the energy of endothermic electrolysis reactions.

The process comprises five basic steps:

i. sunlight harvesting and concentration,
ii. electron/hole separation and electronic charge transfer driven by superbandgap energy in the photovoltaic,
iii. transfer of sub-bandgap and excess super-bandgap radiation to step up heat to the electrolysis chamber,
iv. high-temperature, low-energy electrolysis forming energy-rich products, and
v. cycle completion by preheating of the electrolysis reactant through heat exchange with the energetic electrolysis products.

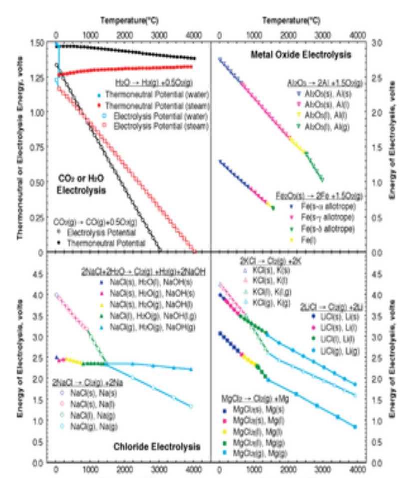
> *Solar heating can decrease the energy to drive a range of electrolysis processes. The electrochemical driving force for a variety of chemicals of widespread use by society will be shown to significantly decrease with increasing temperature...As an example of the STEP solar energy efficiency gains, this study focuses on CO_2 splitting potentials....these potentials (black circles in the figure [at right]) decrease more rapidly with temperature than those for water splitting, signifying that the STEP process may be readily applied to CO_2 electrolysis.*
>
> —Licht, 2009



Calculated potential needed to electrolyze carbon dioxide or water. The indicated decrease in electrolysis energy, with increase in temperature, provides energy savings in the STEP process. High temperature is accessible through excess solar heat. Licht, 2009.

A molten carbonate bath electrolysis cell, fed by CO_2, generates CO—an important syngas component and, which when reacted with H_2, forms methanol. Molten alkali carbonate electrolyte fuel cells typically operate at 650 °C. Licht plans a follow-up study to present experimental measurements of the CO_2 splitting electrochemical potential (to CO or solid C), with increasing temperature.

> *In addition to the removal of CO_2, the STEP process is shown to be consistent with the efficient solar generation of a variety of metals, as well as chlorine, in place of conventional industrial processes. In total, these processes are responsible for the majority of anthropogenic CO_2 release, and their replacement by STEP processes will end the root cause of anthropogenic global warming.*
>
> *The STEP process occurs at solar energy conversion efficiency greater than attainable by photovoltaics alone. This study provides a path for a transition beyond the fossil fuel, electrical or hydrogen economy, to a renewable chemical economy based on the direct formulation of the materials needed by society.*
>
> —Licht, 2009



Calculated potential to electrolyze selected oxides (top) and chlorides (bottom). The indicated decrease in electrolysis energy, with increase in temperature, provides energy savings in the STEP process in which high temperature is provided by excess solar heat. Licht, 2009. Click to enlarge.

Resources

- Stuart Licht (2009) STEP (Solar Thermal Electrochemical Photo) Generation of Energetic Molecules: A Solar Chemical Process to End Anthropogenic Global Warming. *Journal of Physical Chemistry, C*, in press. doi: 10.1021/jp9044644

SCIENCE NEWS
THE WEEKLY NEWSMAGAZINE OF SCIENCE

Tapping sun's light and heat to make hydrogen

Environmentally friendly fuel cells may someday power most cars, homes, and industries. Yet the energy they supply won't be all that clean if the hydrogen that the fuel cells consume derives from fossil fuels. So says Stuart Licht of the University of Massachusetts in Boston, who leads a U.S.–Israeli team of researchers that has demonstrated a new solar-powered way to produce hydrogen from water.

Typically in solar-based electricity generation, only a fraction of the sun's visible and ultraviolet light produces electrons with sufficient energy to split water into hydrogen and oxygen. In the new method, the researchers first use the sun's infrared radiation to heat molten sodium hydroxide mixed with water to oven temperatures that prime the water molecules to break apart.

Under these conditions, even electrons with too little energy to split water molecules at ambient temperatures cleave the heated ones. Thus, hydrogen could be produced using widely available silicon photovoltaic cells, Licht says.

In the Dec. 8, 2003 *Chemical Communications*, Licht and his colleagues report that the new approach achieves a hydrogen-production efficiency of 30 percent and has the potential to do even better. Another Licht-led team held the previous efficiency record of 18 percent using specialized solar cells (*SN: 9/16/00, p. 182*). —P.W.

JANUARY 17, 2004 p. 46, VOL. 165, No. 3

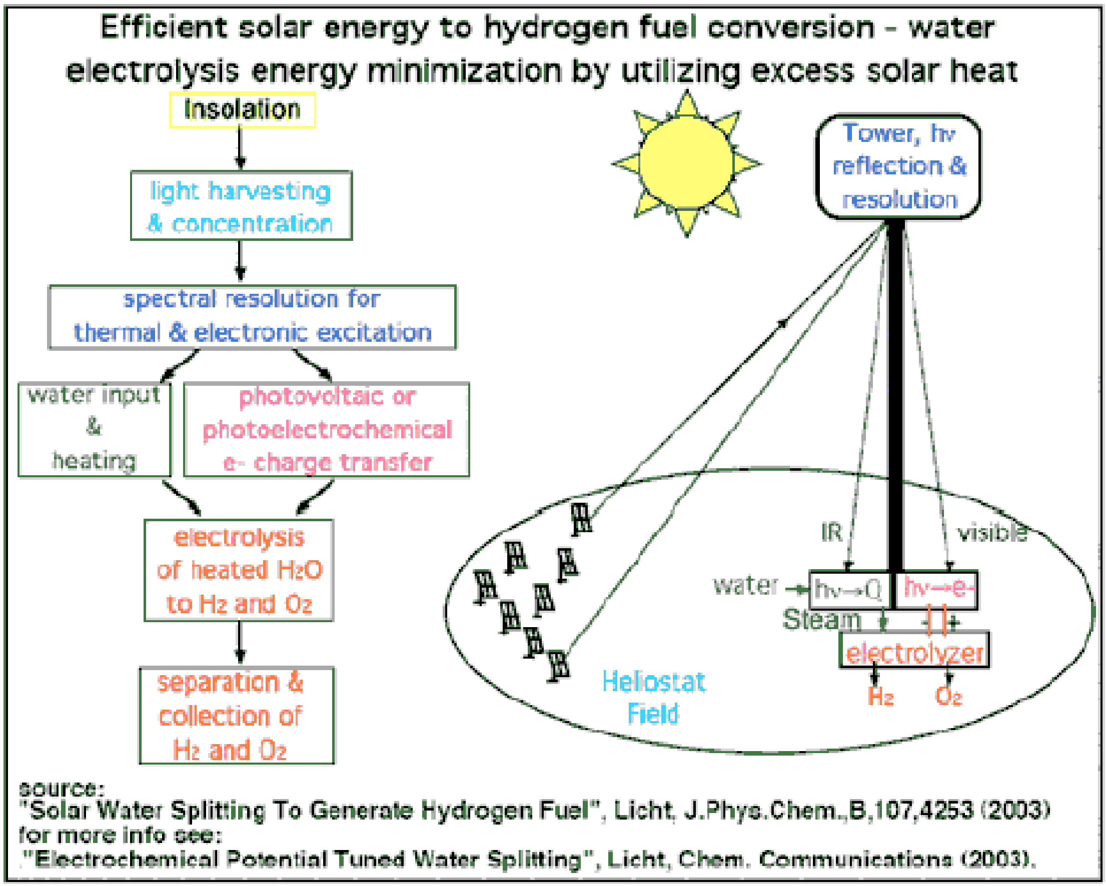
Latest Advances in Hydrogen

California Hydrogen Business Council

THE HYDROGEN CENTURY BEGINS!

December 3, 2003

Solar Hydrogen Fuel Production



HOT! ***"This is a fundamental step in hydrogen production. This confirms that we can create tremendous amounts of hydrogen simply by using solar energy and water. ...We're heading toward a society that uses clean hydrogen as its primary fuel, and that's wonderful."***

Professor Stuart Licht, University of Massachusetts

Shedding New Light on Fuel Cells

Amit Asaravala Wired **December 2,2003**

Unlike current solar hydrogen generators that only make use of the electrical portion of light particles, the UMass process also harnesses the thermal energy produced by the infrared portion of the spectrum. This energy is used to heat the water to 600 degrees Celsius, at which point it is injected into an alkaline solution and then forced to split into hydrogen and oxygen molecules using electrical energy. ...A paper detailing the new technique is scheduled to appear in a December issue of *Chemical Communications*.

www.businessweek.com
BusinessWeek
OCTOBER 23, 2000
A PUBLICATION OF THE McGRAW-HILL COMPANIES

Developments to Watch

EDITED BY OTIS PORT

New York; October 23, 2000; Otis Port; Page: 101:

The Key to Cleaner Fuel Cells? It's in the Water

FUEL-CELL-POWERED CARS and trucks promise to relegate today's pollution-belching engines to the scrap hep7ap. Bigger fuel cells could do the same for coal-fired power plants and industrial furnaces. To get the maximum environmental benefit, though, fuel cells should be fed hydrogen fuel, not gasoline, natural gas, or the other alternatives used by most of the fuel cells now on the market or under development. Chemically converting hydrogen into electricity with a fuel cell produces no pollution, only water.

Unfortunately, there's scant infrastructure for distributing hydrogen, so it isn't practical for cars. But suppose the gas could be produced locally, on demand, from ordinary water. Splitting water molecules into hydrogen and oxygen has long been possible--just not economical. Now, a small Israeli-German-Japanese research team led by Stuart Licht, a professor of chemistry at the Technion-Israel-Israel Institute of Technology in Haifa, is closing in on what could be a commercially feasible way to tap water for its hydrogen--by using sunlight.

Licht's team reports in the Sept. 14 issue of the Journal of Physical Chemistry B that it has developed a system based on a photovoltaic device, or solar cell, that is 18.3% efficient at splitting water molecules. That's a 50% improvement over the previous best--and might be on the threshold of being viable for the corner filling station. But if 18.3% won't do the trick, the researchers believe further refinements could substantially boost the efficiency of their water-splitter, perhaps to as much as 31%.

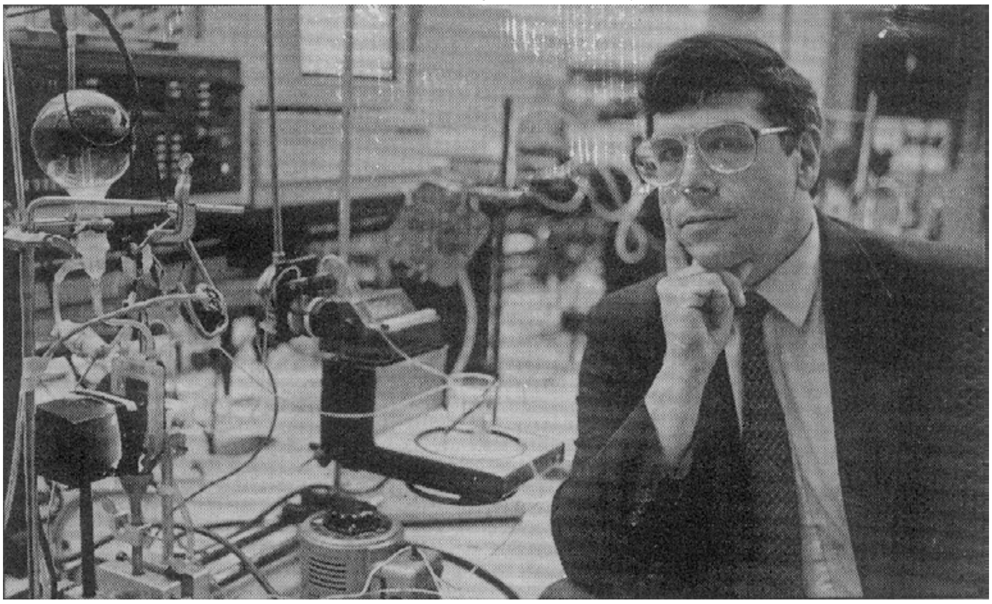
Chemical & Engineering News
SCIENCE/TECHNOLOGY CONCENTRATES
October 2, 2000
Volume 78, Number 40

SOLAR CELL SPLITS WATER WITH RECORD EFFICIENCY

A team of scientists has developed a solar photovoltaic-electrolysis cell that splits water into hydrogen and oxygen with 18.3% conversion efficiency. The system consists of a photovoltaic sensitizer with a layered composite of aluminum gallium arsenide and silicon semiconductors to harvest visible light and an electrolysis component with a platinum black or RuO_2 electrode to catalyze water splitting [J. Phys. Chem. B, 104, 8920 (2000)]. Generation of clean hydrogen fuel with 18% solar energy conversion efficiency is unprecedented, according to team leader Stuart Licht, chemistry professor at Technion--Israel Institute of Technology, Haifa. "We have also calculated that [such] systems are capable of attaining over 30% solar photoelectrolysis conversion efficiency," he tells C&EN. "Previous models predicted that only 16% conversion was possible, and, until now, only 12% efficiency has been achieved experimentally." The group achieved the record efficiency by matching the maximum solar energy photopotential of the photovoltaic sensitizer with the water electrolysis thermodynamic potential and by using an electrolysis component that is very large compared with the sensitizer.

SUNDAY TELEGRAM

SUNDAY TELEGRAM, NOVEMBER 29, 1992



Stuart Licht in the laboratory.

Liquid solar cell can store power

By John J. Monahan
Staff Reporter

> "It's not every day that we double the voltage. But every day we gain an increment of knowledge."
>
> STUART LICHT

WORCESTER — Rainy days don't bother Stuart Licht, one of the world's leading solar energy researchers, so much anymore.

The 38-year-old chemist smiled as he looked out his office window at Clark University on a rainy November afternoon, noting that clouds and nightfall — once primary obstacles — are no longer a barrier to future widespread use of solar energy.

Four years ago, he and his research team at Clark University created the world's first solar electric cell that works in the dark.

The liquid photo-electrochemical cells that Licht and his research assistant, India-born Dharmasena Peramunage, are developing are unlike the conventional solid state solar cells found in calculators and spacecraft. The new cells not only convert light to electricity, but can store some of the power internally, discharging stored power automatically when the light source is removed.

That is but one of the marvels of the liquid solar cell technology Licht and Peramunage are pioneering in a small one-room laboratory at the college's Sackler Science Center.

The palm-sized cells also produce hydrogen as they work, a clean-burning fuel that can be used to power cars.

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Chemist is unlocking the secrets of solar power

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In the last four years, tedious experimentation has led to one breakthrough after another, bringing the technology giant steps toward Licht's dream of making solar power available for widespread use as a clean and inexpensive power source for the future.

The first viable liquid chemical solar cells were discovered in 1976 simultaneously in three laboratories in the United States and Israel. Since then, Licht has been one of the few chemists in the world who has continued developing their potential.

In 1985, he boosted the rate the liquid cells convert light to electrical energy to 12.7 percent of the energy contained in sunlight.

In 1986, his modifications allowed a 100-fold improvement in the operating lifetime of the cells, overcoming what previously had been a major shortcoming of the technology.

In 1987, experimentation aimed at overcoming the intermittent nature of solar energy produced the cell that stored energy and could provide power in the dark, and other modifications boosted the efficiency of the cells to 15 percent.

Two years ago, their research produced even more dramatic results.

As Licht explained it, efforts to boost efficiency focused on alterations of the liquid electrolyte used in the energy conversion process. They had found one type of liquid was breaking down into impurities producing bizarre results in their tests.

At that point, he said, the research team decided to use just the supersulphides that had been causing the problem in the previous experiments.

"In science, sometimes you get the best results from looking at the deviant factors," Licht said of that effort. The odd test with what had been a bothersome impurity produced record-breaking voltage from the cell.

In 1990, the results were published in the British science journal Nature, crediting Licht and Peramunage with a world "solar cell best" achieving an efficiency of 16.4 percent and a world record solar cell voltage of 1.2 volts.

While that is the equivalent of voltage found in a small flashlight battery, it is almost twice that ever stored by any solar cell. Meanwhile the 16.4 percent efficiency achievement equals that of conventional solid state cells that operate at lower voltage, and do not hold the other advantages of the liquid cell technology.

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The laboratory where Licht and his team, which includes Peramunage, four graduate students and two undergraduates, have developed the solar breakthroughs belies the vast significance their research could have for the world.

The Sackler Science Center lab is about the size of a large bedroom, with some older looking chemical mixing hoods in the corners, two long lab benches in the middle with homemade computers and video screens on the shelves, and the kind of tubing and burners typical of a school chemistry lab.

The roof of the four-story building has become the proving ground for their solar cells.

Licht said the scale of the operation provides its own advantages with a freedom to test out new ideas as they occur to the team.

What they lack in funding, compared to large multi-million dollar research centers, he said, they are often able to make up by designing their own equipment. The team built their own water purification system and when they needed a computer that could make as many as 50,000 measurements per second, they rigged up their computers to do the job.

> "We have a chance to wrestle with the secrets of the universe. It's a very fulfilling life. I can't see how anyone who has an opportunity to find a piece of information no one else has ever had could pass it up. I can't see why anyone would do anything else."
>
> STUART LICHT

In his mind, the quality of the science doesn't always depend on spending.

"Some scientists follow the money, I follow the dream," Licht said. "We have done substantial electro-chemistry here for several years now for less than $100,000 per year."

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Behind Licht's success is a complete command and fascination with chemistry.

He displays confidence in his ability to unravel mysteries of the physical world when he talks about his work, and seems to revel in the challenges. Chemistry has always been the focus of his life.

He was born in West Roxbury into a family of chemists.

His grandfather, the late Joseph Licht, worked as a bench chemist for Stanley Tools in Connecticut and sent Stuart's father, Truman S. Light, through Harvard. His father taught chemistry at Boston University when Licht was growing up. His mother, Arlene Light, is an industrial chemist for the Kendall Co.

His routine is one of 14- and 16-hour days, working 12 days at the campus and spending two days off with his children at his home in a quiet section of Charlton.

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The basic challenge of Licht's research is to understand what happens to a photon or light particle when it comes into contact with the semiconductor of the solar cell and frees an electron to produce electricty.

Licht published the first explanation of that process in the chemical solar cell in Nature in 1987 and remains focused on the phenomena.

It happens in billionths of a second, but for him the challenge is to identify what is slowing that process so that only a fraction of the light energy is converted. If he can find a way to speed it up, by testing endless options for combinations of materials, temperature and other conditions, he knows he would be able to boost the energy-producing efficiency of the cell.

"It's not every day that we double the voltage. But every day we gain an increment of knowledge," Licht said.

"We have a chance to wrestle with the secrets of the universe. It's a very fulfilling life," he said, "I can't see how anyone who has an opportunity to find a piece of information no one else has ever had could pass it up. I can't see why anyone would do anything else."

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After nearly two decades of dedicated research, Licht now believes it is time for solar technology to move from the lab to applications research.

Licht noted that the government cut off funding for liquid solar cell research in 1985, effectively ending research that was ongoing at the Wiezman Institute of Science in Israel, Bell Laboratories, and Massachusetts Institute of Technology, where the first viable electrochemical solar cells were simultaneously discovered in 1976.

Since then he said the only scientists continuing to explore the chemical side of solar energy have been a small group at California Institute of Technology and his team at Clark.

"Primarily it has been Clark University's belief in these cells that has kept the research going," Licht said.

Currently the team is working on a project to develop a new type of battery for use with the liquid cell. Licht also has plans to attempt other breakthroughs.

"I would like to break the world's record for the amount of energy we can get out of electro-chemical materials," he said.

He also hopes to accelerate ions to near light speed, something that has never been done before. "That would open up a new realm of chemistry," he said.

SCIENTIFIC AMERICAN

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LIQUID SOLAR CELLS

Chemist Stuart Licht of Clark University in Worcester is developing a liquid solar cell capable of converting more of the sun's energy to electricity and of producing a voltage twice as high as that of conventional photovoltaic cells. Liquid solar cells can be adapted to store energy for use when there is no sunlight and also can generate valuable chemical byproducts, such as hydrogen, which can be used to run cars without pollution.

Licht's liquid solar cell is compact enough to hold in the hand. It consists of two electrodes immersed in a chemical solution. Energy is generated when a semiconductor is hit by sunlight, generating a stream of both electrons and chemicals. The electrons then flow through a wire, from which a current can be tapped. After the energy is tapped, the electrons flow back into the solution and return to the semiconductor, insuring continued energy.

THE WALL STREET JOURNAL.

MARKETPLACE

Solar Cells That Hum After the Sun's Gone

WITHIN a few years, solar cells may be available that work in the dark.

The photoelectrochemical cells resemble a cross between the familiar solid-state solar cells that convert light to electricity and old-fashioned, wet-cell batteries. They combine semiconductors, which make electricity when hit by light rays, with electrodes bathed in electrolytes, which enable the cells to be charged up like car batteries.

In bright light, the cells both make electricity and recharge. In low-light conditions, their stored energy can be tapped. The combination promises a leap forward for nonpolluting solar power, which has been hindered by its intermittent nature.

Researchers have faced formidable problems making PEC cells practical, though. Their semiconductors have tended to corrode quickly. And the cells' efficiencies—the proportion of light energy converted to the electrical kind—have been relatively low compared with solid-state alternatives, which have reached 25% efficiency in laboratory tests.

Recently, a team led by chemist Stuart Licht at Clark University in Worcester, Mass., has made steady progress in overcoming the problems. By fine-tuning levels of electrolyte constituents, the team has achieved efficiencies of about 17% in PEC cells that work for weeks. "The exciting thing now," says Mr. Licht, "is that there are theoretical indications liquid solar cells can access more of the sun's energy than solid-state cells can."

Several companies have expressed interest in the technology, which may lead to commercial cells in a few years, he adds.

Monday 3 September 1990 London THE INDEPENDENT

A cheaper way to touch the sun

Lionel Milgrom explains a revolutionary solar cell that improves the efficiency of converting sunlight into energy

AMERICAN chemists could be close to converting sunlight into a cheap source of energy. Dr Stuart Licht and a team from Clark University in Worcester, Massachusetts, are perfecting a new solar cell that works like a conventional battery as it converts sunlight into electrical power.

The more familiar solid-state solar cells or photo-voltaic devices (which produce electric current at the junction of two substances exposed to light), are found in spacecraft and calculators. These are highly developed and efficient, but relatively expensive to produce. This makes them too costly to generate solar electricity on a large scale, even though solar power would not contribute to global warming. The new device, called a photoelectrochemical cell, though less efficient than solid-state devices, is much cheaper to make. These cells could pose a serious challenge to the supremacy of solid-state devices for solar energy conversion.

Turning the sun's light into chemical energy is not new. For billions of years, photosynthesis has provided the basic chemical driving force for practically all life on earth. Plants convert sunlight, carbon dioxide and water into high-energy carbohydrates, liberating oxygen in the process.

From an industrial point of view, though, photosynthesis is highly inefficient. On average, only 1 per cent of sunlight is converted into energy-yielding compounds such as wood. For an industrial society, such a low efficiency would mean turning over vast tracts of land to solar energy conversion.

The most promising approach so far to solar energy seems to be to convert sunlight directly into electricity. Up to now, this has meant moving away from chemistry and biochemistry and into the realms of solid-state physics.

When light shines on a semiconducting material, it "knocks" electrons out of the outer orbits of the atoms of the material and so generates an electric current. But there is a snag. The conductivity is short-lived. Physicists tackle this by grafting on another piece of semi-conductor with a slightly different structure. Where the two semi-conductors meet is called a p-n junction and the effect is to keep the current flowing for as long as light falls on the device.

These cells are reliable and highly efficient — the best laboratory models work at 25-26 per cent efficiency. But they are expensive to make: fashioning the all-important p-n junction requires all the skills of modern electronics technology.

The photoelectrochemical cell has been developed to help solve the problem. Chemists have put the semi-conductor in contact with an electrolyte — a water-based solution which has the same effect on the semi-conductor as the p-n junction.

The electrons knocked off the atoms of the semi-conductor by the light pass this time into the electrolyte, rather than into another piece of semi-conductor. The effect is rather like what happens at one terminal of a battery. If another electrode is placed in the electrolyte, current will flow through a completed circuit outside the cell, from semi-conductor to electrode. This is the photo-electrochemical cell: to generate a current just shine light on the semi-conductor.

Photoelectrochemical cells could also produce chemical fuels. The passage of an electric current through a water-based electrolyte causes chemical reactions at one of the electrodes, producing hydrogen. This can be burnt or stored for later use.

The chemical cells are also cheaper than photo-voltaic devices. The semi-conductor electrode does not need the hi-tech treatment used in making silicon solar cells. The problem is that the chemical reactions started by the semi-conductor can dissolve it.

This is called photo-corrosion, a light-induced rusting which eats away at the semi-conductor and covers it with an electrically insulating layer. This drastically reduces the life-span of the cell, sometimes to the order of seconds. Moreover, the chemical cells are less efficient in turning light into electricity than the photo-voltaic ones.

In the early Eighties, chemists were so gloomy about the prospects for these cells that they were predicting efficiencies of about 10 per cent by the late Nineties. But in 1984, Nathan Lewis of Stanford University in California smashed the 10 per cent barrier by using electrolytes that did not contain any water. This beat the corrosion problem but at a price: no water must be let into the system. Later, Lewis was able to hoist the efficiency of his cells to 15 per cent in water-based electrolytes by coating his semi-conductor, made from gallium arsenide, with an ultra-thin film of expensive osmium.

Now Stuart Licht has gone one better. He has used a special combination of semi-conductor (this time cadmium selenide, which is cheaper than gallium arsenide and which reacts to light differently) and a water-based electrolyte. This enables the cell to produce its maximum operating efficiency — a new high at almost 17 per cent — over days instead of seconds.

Apart from being much cheaper to make than a solid-state solar cell, Licht's new cell does something that no solid-state cell can do. It generates a comparatively high voltage — 1.2 volts (about the same as a conventional torch battery), compared to only 0.7 volts from a silicon solar cell. "There is no reason why we shouldn't get even higher voltages in the future, which will lead to efficiencies that easily rival those from solid-state devices," he says. Because photo-electrochemical cells, unlike photo-voltaic devices, can also store solar energy, which neither contributes to global warming nor world pollution, large-scale solar power generation could one day compete with nuclear power and fossil fuels.

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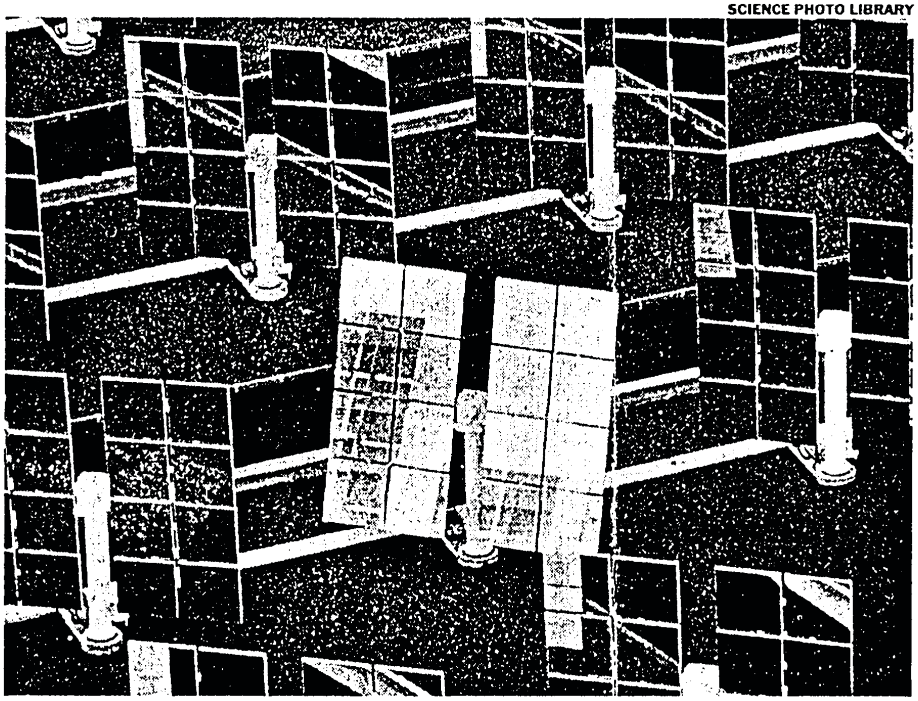
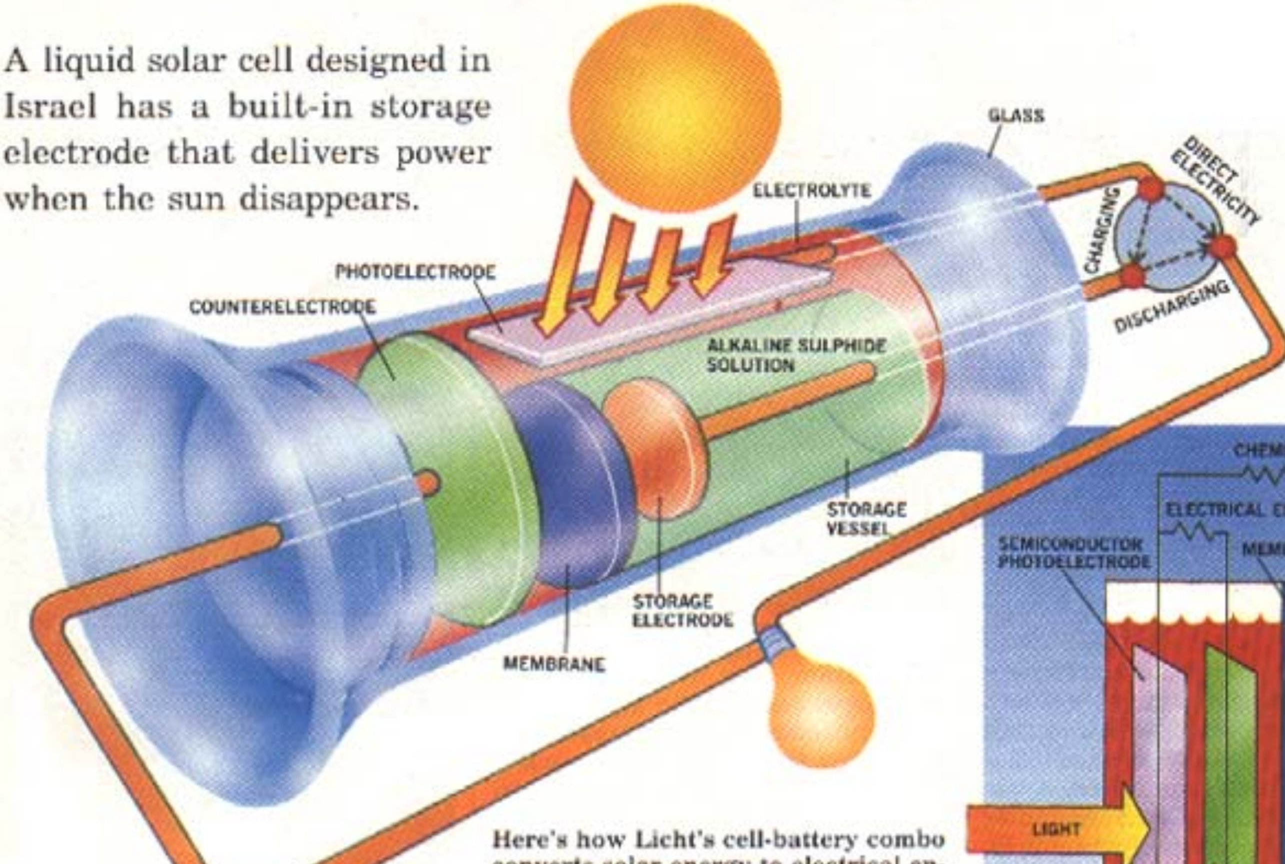


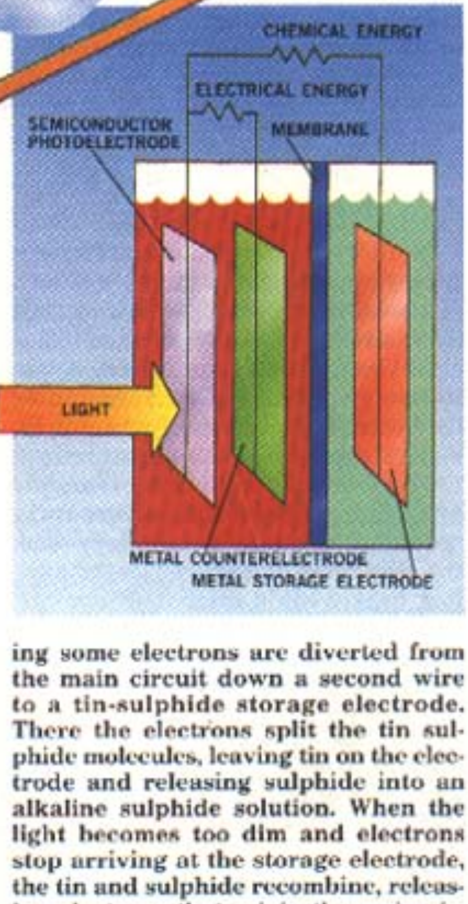
Solar cells at Adrano in Sicily: conventional systems do not harm the environment but need vast areas of land

SCIENCE is edited by Tom Wilkie

Solar cell that works nights

A liquid solar cell designed in Israel has a built-in storage electrode that delivers power when the sun disappears.





Here's how Licht's cell-battery combo converts solar energy to electrical energy: A lone crystal of cadmium selenide telluride, a semiconductor, serves as a photoelectrode. It's immersed in a solution of aqueous polysulphide, an electrolyte. A cobalt sulphide counterelectrode, also immersed in the bath, is wired to the photoelectrode. Light hitting the photoelectrode excites electrons, which then jump from the electrolyte. They travel from the photoelectrode to the counterelectrode, powering an electrical device placed along the wire connecting the two electrodes. Upon reaching the counterelectrode, the electrons return to the electrolyte, completing the circuit.

In Licht's device solar energy also drives a chemical reaction to stockpile chemical energy. While the sun is shining some electrons are diverted from the main circuit down a second wire to a tin-sulphide storage electrode. There the electrons split the tin sulphide molecules, leaving tin on the electrode and releasing sulphide into an alkaline sulphide solution. When the light becomes too dim and electrons stop arriving at the storage electrode, the tin and sulphide recombine, releasing electrons that rejoin the main circuit and deliver power.

By DAWN STOVER
Drawings by Bob Lange

"One of the biggest problems with solar energy is its intermittent nature," says Dr. Stuart Licht, a chemistry professor at Clark University in Worcester, Mass. "It's not useful to a normal household."

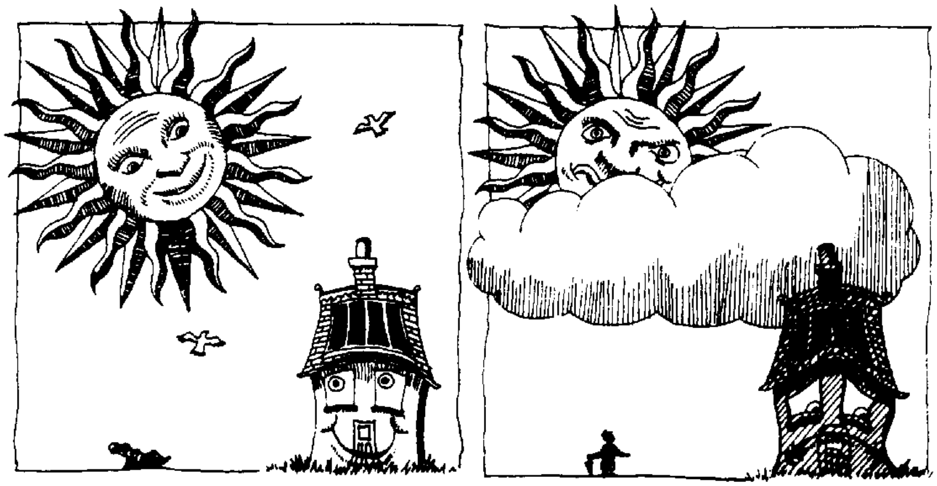
While at the Weizmann Institute of Science in Rehovot, Israel, Licht and a group of researchers came up with a solution: a device that captures *and stores* solar energy. It discharges electricity in the dark.

Shortly after liquid solar cells containing conductive chemical baths were invented in the late 1970s, the Weizmann team suggested these cells could incorporate storage batteries. "We already had an electrochemical system," says Licht. "And a battery is also an electrochemical system."

Other solar researchers, trained in solid-state physics, hadn't figured out how to prevent light-induced rusting. "I approached the problem purely as a chemist," Licht says. Instead of looking for protective coatings, he sought chemically compatible materials that would react in constructive ways—circumventing more destructive pathways.

The cell-battery system's overall efficiency is 11.3 percent, slightly better than a photovoltaic cell combined with an external battery.

Licht is now experimenting with inexpensive thin-film photoelectrodes. If its efficiency can be improved, a thin-film system could provide round-the-clock energy for remote areas. PS



Solar cells

Mehr Licht

CAMBRIDGE, MASSACHUSETTS

SOLAR cells are fair-weather friends. The conventional sort, known as solid-state photovoltaic cells, can heat and light a house, but only while the sun shines. An external storage battery can ensure a supply of power on overcast days, but it defeats the object of solar cells. They are supposed to make electricity cheaply.

Another, less familiar system promises to make electricity from the sun even when it is not shining. This is the liquid solar cell. Like its solid-state cousin, it uses semiconductor material that is sensitive to light. Instead of being combined with other solid materials, the semiconductor is immersed in an electricity-conducting chemical bath. This forms a "photoelectrode". Sharing its bath, and attached to the photoelectrode by an external wire, is a second, counter-electrode. When light hits the photoelectrode, reactions at its surface remove electrons from the bath. The electrons move along the wire to the counter-electrode. This motion can be used to power an electrical device, or "load", along the way.

When they reach the counter-electrode, the electrons return to the chemical bath, thus regenerating it. (Depending on the materials used, the electrons may instead move from the counter-electrode to the photoelectrode; and the bath may be a gel rather than a liquid.) Since a storage battery also consists of electrodes immersed in electrochemical solutions, it should be fairly simple to incorporate a battery into a liquid solar cell—thus giving continuous power.

Liquid solar cells have not yet come into their own. First, they do not yet turn sunlight into electricity nearly as efficiently as solid-state cells do. Second, the same chemical reactions that make them work also dissolve them. And, it is hard to find to find a storage battery that is chemically compatible with them.

According to Dr Stuart Licht, who is now at the Massachusetts Institute of Technology, the problem was that nobody really understood the liquid solar cell. Hundreds of studies examined what happens in and on the semiconductor; nobody paid much attention to the chemicals in the bath. During some experimental work at the Weizmann Institute of Science at Rehovot in Israel, Dr Licht identified 15 chemicals in a typical electrochemical bath and worked out how each one did its job. He spotted two chemical processes that limited the conversion efficiency of the cells (that is, the amount of power coming out when a certain amount of sunlight goes in).

This knowledge let him and his colleagues make some improvements to one promising type of liquid solar cell. In their version, the photoelectrode is a single crystal of cadmium selenide telluride, the counter-electrode is cobalt sulphide and the solution is an aqueous polysulphide. The conversion efficiency of the new polysulphide cell is almost 13%—nearly double the old version's best performance. With improved performance comes another bonus: a hundred-fold reduction in corrosion.

A conversion efficiency of 13% is good for a liquid solar cell, but it is only half the maximum achieved by a solid-state device while the sun shines. Fortunately, Dr Licht and his team have also found a type of storage battery that works well with their liquid solar cell. They use a tin-sulphide electrode in an alkaline-sulphide solution, separated from the rest of the cell by a permeable membrane. A wire from the "storage" electrode joins the main circuit between the photoelectrode and the load. When the sun shines, some of the electrons go down the wire to the storage electrode instead of along the main circuit and through the load. Those electrons split the tin sulphide molecules, leaving tin on the electrode and releasing sulphide into solution.

When the incoming light dims and electrons no longer arrive at the storage electrode, the tin and sulphide spontaneously recombine, releasing electrons that were captured before. Unable to flow back to the photoelectrode, the electrons rejoin the main circuit and flow through the load to the counter electrode. Averaging over day and night, Dr Licht's solar cell with a built-in storage electrode yields a conversion efficiency of 11.3%. This beats the record for solid-state systems with external batteries. Also, it needs no electronic switching or computer control to link the battery and cell. The cell simply stores energy and releases it spontaneously when it is needed. Despite fluctuating amounts of sunlight, the power provided is almost constant.

Similar cells can produce fuels or chemical products instead of electricity. For example, electrons escaping from the storage electrode split water into oxygen and hydrogen gas, a clean fuel that can be bubbled off. For continuous supply, add more water.

Dr Licht is the first to point out that problems remain. The photoelectrode in his cell is a single crystal. Systems that use photoelectrodes made of thin films are markedly cheaper because they are easier to make, and more durable, but also less efficient. There are already signs that what he has learnt about the chemistry of such cells will help. Dr Licht has raised the conversion efficiency of one thin-film system from 4% to 6% (when illuminated) and extended its lifetime from months to years. Although liquid solar cells are still, for the most part, creatures of the laboratory, the closer they are examined the more promising they look.