FROM THE LABS

Game-changing redox flow battery

Researchers at Indian Institute of Technology, Madras, have developed a 'vanadium redox flow battery' (VRFB) through a project funded by ONGC Energy Centre Trust and the Pudukkottai-based company High Energy Batteries. Redox flow batteries (RFB) promise to become a game-changer for future energy storage systems in the stationary segment.

Dr Kothandaraman Ramanujam of the Department of Chemistry at IIT-Madras notes that "adopting VRFB into the energy distribution chain will ensure continuous power supply from wind and solar farms. Since it utilises an aqueous electrolyte, it is safe and does not get affected by thermal runaway issues. Besides, this can be used as large-scale UPS [uninterrupted power supply] for office buildings".

Transporting the charged electrolyte to remote locations, just like a tanker carrying petrol, will help generate electricity onsite using a simple pumping mechanism without need for the complicated engines used in power generators.

Ramanujam's team successfully demonstrated 1kW/10kWh VRFB using solar power charging. More than 300 cycles (each cycle takes about three days) have been completed using solar charging. The developed VRFB can operate at a high current density with 80-85 per cent efficiency.

Currently, an ion-conducting membrane, called 'Nafion,' is used in the VRFB stack. This constitutes nearly 25 per cent of the system cost. The research group is looking into developing cost-effective ceramic-hydrocarbon-based porous membranes in place of Nafion, says a statement from IIT-Madras. In order to further reduce the cost of RFB, alternatives to vanadium, based on lead and organic redox materials, are being explored.

The group is also working on alternative flow battery chemistries that use abundantly available lead, zinc, iron and organic redox-active materials. This would bring down the cost of energy storage on par with or lower than the cost of energy production from solar photovoltaics. Currently available energy storage options are more expensive than the cost involved in generating electricity.

Break an egg to fix a tooth or two

Non-toxic and plentifully available, eggshells promise to be the perfect raw material for bioceramics — bone and dental fillers

M RAMESH

If the stakeholders play it right, we could see the birth of a new industry whose essential raw material is something that is dumped as waste — eggshells.

In recent years, the scientific community has been discovering the usefulness of eggshells in making bioceramics — materials used to repair bones and teeth. Eggshells, non-toxic and plentifully available at practically no cost, are rich in calcium carbonate, which can be converted into a variety of calcium phosphates, the basic building material of bones and teeth. Recent research by Prof TS Sampath Kumar of the Medical Materials Laboratory, Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Madras, identifies several pathways for the use of eggshell-derived chemicals in medicine — as bone fillers, dental fillers, cements and drug delivery systems.

This is of particular interest to India, home to the world's third largest poultry sector, where 730 million birds lay about 120 billion eggs a year — roughly, 600,000 tonnes of eggshells. Kumar calls it a 'gold mine'.

His research, published in the *Journal of the Indian Institute of Science*, tried to find out why eggshells are so suited to be made into bioceramics. When a doctor injects a paste into a fractured bone, it is expected to bond with the bone environment and become a part of it. Basic chemistry tells us that any bonding involves the attraction of ions, which are atoms that have more electrons than protons (negatively charged) or fewer (positively charged). So, proper bonding calls for the presence of ions. Bones have tiny amounts of magnesium, strontium, silicon and sodium. Kumar's research showed that eggshells, too, have these. In fact, without these, the birds couldn't have made the eggs in the first place.

Eggy gold India is home to the world's third largest poultry sector ISTOCK.COM

Cooking up a solution

Eggshells are made up of calcium carbonate (94 per cent), calcium phosphate (1 per cent) and other organic matter (4 per cent). Calcium phosphates (CaPs) have been known to be good bone substitutes. Among the various CaPs, hydroxyapatite (HA) and its variant, calcium-deficient hydroxyapatite (CDHA), are known to help bone healing and bone regeneration.

Kumar's Medical Materials Laboratory is tucked away in a nondescript, tiled shed that once used to house electrical generators. It has none of the glitzy sophistication of a buzzing chemical research centre. But, as it turns out, the researchers here didn't need anything more than a ream of writing paper and a microwave oven.

Using the microwave oven, Kumar and his team (comprising K Madhumathi and R Jayasree) synthesised HA and CDHA from cleaned chicken eggshells. (Eggshells were heated to 900 degrees C for three hours to convert calcium carbonate into calcium oxide, which, in turn, becomes calcium hydroxide on exposure to air. Adding diammonium hydrogen phosphate to this yielded nano CDHA).

The process was novel — it was indeed a sort of cooking, with eggshells and phosphoric acid. The team was also able to 'tune' the CDHA to vary the ratio of calcium to phosphorous for application-specific compositions.

While CDHA is a sort of flagship product, the team came up with a bunch of other products too. For example, they heated HA to 1,100 degrees C, and came up with tricalcium phosphate (TCP). Heat HA to 1,400 degrees C, you get tetra-calcium phosphate (TTCP), an excellent material for making cement to fix broken bones.

The nano carriers

Further, any material that is introduced into the skeletal system to fill gaps or build back bones or gum together broken bones should ideally be capable of conducting drugs to wherever they are required. For example, if there is a bone infection, the man-made material should be a good drug carrier. Kumar says eggshell-derived materials are good at this too. It is not difficult to synthesise calcium phosphate in nano form. Nano materials distribute drugs well. Calcium phosphate nanoparticles offer more reaction sites for drug binding due to their high surface-to-volume ratios compared with bulk form. The researchers found out that eggshell-derived nano CDHA, tuned to a calcium-to-phosphate ratio of 1.61, was best suited for delivery of antibiotics, while eggshell-derived TCP was best for ibuprofen loading.

Thus, the team was able to produce a phalanx of products from eggshells, such as HA, CDHA (with variable calcium-to-phosphate ratios), carbonated apatite, amorphous calcium phosphate, TCP and TTCP, to suit specific medical applications. Kumar stressed that many more products could be derived from eggshells — any calcium-based product. For example, carbonated apatite, a good cancer fighter, can be produced from eggshells.

It is pertinent to note that calcium phosphates have always been used for bioceramics. What's new is that it can be made from eggshells. Kumar notes that people generally keep away from natural raw materials because they are non-homogenous. For instance, different eggshells from different parts of the country could have varying properties. The solution is to procure eggshells from a single source. On the other hand, eggshell-based bioceramics are better than synthetic bioceramics because they contain ions of magnesium, strontium, silicon and sodium. "The various ions present in eggshell can not only play a key role in bone regeneration but also influence the binding of therapeutic molecules like proteins and drugs," Kumar says.

He says that the research is at a technology readiness level of 4 (TRL-4), which means it is ripe for the industry to scale it up. Further, the use of eggshells is still under-explored — there would be many more specific applications. For example, 3D bioprinting with eggshell-derived biomaterials could lead to the fabrication of more functional tissues and organs.

One should also not forget the role of this eggshell-derived bioceramics in the circular economy. Indiscriminate disposal of eggshells leads to microbial contamination, a harm that we hardly take notice of. A push from the government towards collection of eggshells would be a big help, Kumar says.

We value your feedback.
Do send your comments to quantum@thehindu.co.in

MICRO-ENERGY

Bacteria that pack a punch

How the common streptomyces promises to fuel rockets

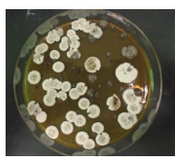
TEAM QUANTUM

Scientists at the US Lawrence-Berkeley Lab have developed a fuel from a bacterium that packs more energy than even the rocket fuels in use today. In fact, the inspiration for the work appears to have come from rocket fuel. Data from simulation show that the fuel has energy density values exceeding 50 megajoules a litre, compared with 32 MJ for petrol and 35 MJ for RP-1, a kerosene-based rocket fuel.

The scientists have named the new fuel 'POP-FAME', for polycyclopropanated fatty acid methyl ester.

LB Lab says that, back in the 1960s, the Soviet Union had developed a petroleum-based rocket fuel called Syntin and used it successfully to launch several Soyuz rockets in the 1970s. Despite its powerful performance, Syntin manufacture was halted due to its high costs and the unpleasant process involved — namely, a series of synthetic reactions with toxic by-products and an unstable, explosive intermediate, says a press release from LB.

POP-FAME's molecular structure closely resembles Syntin's. At the heart of the fuel's structure is the 'three-carbon' ring — a triangle with a carbon atom at each vertex. (Each carbon atom combines with two other carbon atoms and two other elements, mostly hydrogen.) This structure is called a cyclopropane; they hold potential energy in their bonds. The scientists began by wondering if such three-carbon-ring-based compounds, which are extremely inflammable, could be produced through the bio-route, using bacteria.



Project leader Jay Keasling, a synthetic biology pioneer and CEO of the Department of Energy's Joint BioEnergy Institute (JBEI), scoured the scientific literature for organic compounds with three-carbon rings and found just two such materials, both made by a bacterium called streptomyces. (This bacterium is used to make many drugs, including the familiar streptomycin.) One of them had been genetically analysed decades ago due to an interest in its anti-fungal properties. This product, called jawsamycin, has five three-carbon rings. The scientists identified the genes responsible for the enzymes that can make the three-carbon rings and genetically engineered the bacteria to coax it to produce the desired fuel.

POP-FAME is said to have higher energy densities than Syntin, which means even a small quantity of the fuel can pack considerable energy, making it an ideal rocket fuel. The team's next goal is to figure out how to remove the two oxygen atoms in each molecule, which are dead weight.

Since publishing their proof-of-concept paper, the scientists have begun work to increase the bacteria's production efficiency even further to generate enough for combustion testing, the LB release says. They are also investigating how the multi-enzyme production pathway could be modified to create polycyclopropanated molecules of different lengths. "We're working on tuning the chain length to target specific applications," said Eric Sundstrom, one of the scientists in the team. "Longer chain fuels would be solids, well-suited to certain rocket fuel applications, shorter chains might be better for jet fuel, and in the middle might be a diesel-alternative molecule."

However, the scientists haven't yet produced enough fuel for field tests. You'd need 10 kg of fuel for an actual test in a real rocket engine. "We are not yet there," says Pablo Cruz-Morales, one of the members of the team. But the scientists' collaborators at another lab (Sandia National Laboratories) have used computer simulations to estimate how the fuel would perform compared with conventional fuels. They found out that POP-FAME carries more energy than petrol or some conventional rocket fuels.

"Energy density is everything when it comes to aviation and rocketry and this is where biology can really shine," says Corinne Scown, JBEI's Director of Technoeconomic Analysis.

Eventually, the scientists hope to engineer the process into a workhorse bacteria strain that could produce large quantities of POP molecules from plant waste food sources (like inedible agricultural residue and brush cleared for wildfire prevention), potentially making the ultimate carbon-neutral fuel, the LB press release says.

WOW!

Beasts do the math

M RAMESH

In the American anthology film *The Ballad of Buster Scruggs*, one of 2018's big hits, an impresario sees his collections dwindle because of competition from another whose show is a chicken that can perform addition and subtraction. In another episode of the anthology, a gold prospector in a remote wilderness climbs a tree to steal some eggs from an owl's nest, dithers when he sees the bird watch him ruefully from another branch, changes his mind and takes just one egg instead of all, muttering to himself, "After all, how high can a bird count?"

Can animals and birds count? Brian Butterworth says they can.

The author of *Can Fish Count? What animals reveal about our uniquely mathematical minds* is convinced that non-human living beings are not without numerical discrimination abilities. They sure can tell many from few. All kinds of animals discern the difference between 10 and 15, *Discover* magazine quotes Butterworth as saying.

What's the thread count Research shows spiders can perform simple arithmetic processes much like humans ISTOCK.COM

Butterworth experimented by putting a fish in a large tank that had other fish of the same species at one end. He found that some individual fish always swam towards its ilk, while other individual fish didn't. When he put the smart and dull fish together, the dull followed the smart — just as humans do.

Now Butterworth is teaming up with neuroscientists and molecular geneticists to study the genetic mechanisms underlying numerical ability.

Another researcher, Dr Vera Schlussel, at the University of Bonn, has published a study titled 'Cichlids and stingrays can add and subtract 'one' in the number space from one to five', in which she concludes that "the ability to 'count' and to perform simple arithmetic processes is not just present in humans, non-human primates and birds, but also in invertebrates such as honey bees and spiders and in fish.

PATH-BREAKER@100

Lending Goodenough power to the lithium battery revolution

Celebrating the centenarian Nobel laureate John Bannister Goodenough and his ongoing quest for cutting-edge technology

M RAMESH

Today you can hardly imagine a world without lithium batteries. The man who gave them to the world, Prof John Bannister Goodenough, is celebrating his 100th birthday this month.

The 2019 Nobel laureate is a man of his word. In 2015, he told his biographer Steve LeVine, "I'm only 92, I have a long way to go."

Contrary to popular belief, however, Goodenough was not the inventor of lithium batteries. Stan Whittingham, the British-American scientist who shared the Nobel with Goodenough, was the first to postulate that lithium, which can liberally donate electrons for a flow of current, can be stored within sheets of titanium sulphide.

However, Whittingham's cell could never have made it to industry; it caught fire frequently. Goodenough perfected it with a cobalt-based cathode to create a product that today touches nearly everyone's life.

A ton and at the crease, Goodenough is a rockstar of the scientific world, thanks partly to his great student diaspora. Many of them are gathering in Austin, Texas, later this month to celebrate their guru's centenary birthday.

Prof Ramasamy Murugan of Pondicherry University was one of Goodenough's students.

He tells *Quantum* that his teacher's contribution went way beyond lithium batteries. "His work in random-access memory for digital computers and the Goodenough-Kanamori rules for magnetic interactions are equally important to science," Murugan says. Another student, Prof Preetam Singh of IIT-BHU, Varanasi, points to Goodenough's "immense contribution to superconductivity, especially in crossover conductivity phenomena." Goodenough was also the inventor of sodium superionic conductor NASICON, says Singh.

John Bannister Goodenough IMAGE COURTESY: US EMBASSY SWEDEN (WIKIMEDIA COMMONS)

Triumph against odds

What makes Goodenough's achievements particularly noteworthy is the fact that his seminal work came on the back of immense struggles in his personal life, especially during his formative years.

His biographer points out that his childhood was a washout, as his parents squabbled and his mother scarcely took care of him. In school, the young John battled dyslexia, which made it difficult to understand lessons or keep up in the chapel, says LeVine.

"Instead, he occupied himself in explorations of the woods, its animals and plants." Eventually, he overcame his disability to enter Yale and passed out magna cum laude in mathematics.

Later he served the US army during World War II. On his return to academics, his undergraduate teacher at the University of Chicago told him, rather derisively, that at his age other physicists had already achieved their peak.

LeVine gives a detailed account of how Goodenough developed the cobalt cathode and how the technology was stolen by a Japanese student, Shigeto Okada, whom Goodenough had admitted in his class at the behest of Nippon Telegraph and Telephone (NTT). What resulted was a protracted $500-million lawsuit filed by the University of Texas against NTT.

There is a small Indian connection to the episode. Goodenough had put Okada to work alongside an Indian post-doc, Akshaya Padhi. When Goodenough discovered Okada's tech-theft, he asked Padhi to record details in his notebook to be used as evidence in court, but Padhi is said to have refused, saying, "Sorry, he is my friend."

Going by LeVine's account, Goodenough appears to have been continually short-changed by people who profited immensely from his technology, though he seemed unaffected by this. Goodenough has, instead, remained a seeker of knowledge all his life.

Constant search for solutions

Murugan recalls that "even at the ripe age of 90, he used to visit the laboratory and meet each one of the scholars and discuss work, the (technical) problems and possible directions to solve them". He also says that Goodenough "likes India and Indian scholars and we used to discuss a lot about Indian culture". Preetam Singh recalls that when he entered Goodenough's room for the first time, the scientist had asked him, "Where is your turban?" He had explained to tell him that not all Singhs were Sikhs.

Murugan and Singh (as well as LeVine) mention Goodenough's sense of humour and his "unique laugh", a recording of which is sometimes embedded into articles about the man.

Singh observes that Goodenough would make people so comfortable that "you can discuss the most stupid idea with him".

Eight years ago, when he was, in his words, "only 92", Goodenough had been pained to note that lithium batteries had not yet lived up to their potential. He mentioned that he was working on an idea. Nearly a decade on, things have not improved much.

However, recent research in solid state batteries, which feature a solid electrolyte (lithium garnet), holds promise. But the engineering issues around solid-state batteries will most certainly be solved; when that happens, lithium-ion batteries will see universal adoption. This, experts say, could happen in five years. Time enough for Goodenough to witness this — after all, he is only 100.