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WHERE DISCOVERIES BEGIN

Discovery

New, high-energy rechargeable batteries

Researchers develop molten air battery with commercial potential

June 27, 2014

While electric vehicles offer many advantages--including reducing greenhouse gas emissions and the country's dependence on imported petroleum--at least one barrier stands in the way of their large-scale adoption: "range anxiety."

The current 2014 electric Nissan Leaf, for example, has a range of just 84 miles on a fully charged battery.

With support from the National Science Foundation, researchers at George Washington University, led by Stuart Licht, think they have developed a novel solution, and they're calling it the "molten air battery."

These new rechargeable batteries, which use molten electrolytes, oxygen from air, and special "multiple electron" storage electrodes, have the highest intrinsic electric energy storage capacities of any other batteries to date. Their energy density, durability and cost effectiveness give them the potential to replace conventional electric car batteries, said Licht, a professor in GWU's Columbian College of Arts and Sciences' Department of Chemistry.

The researchers started with iron, carbon or vanadium boride for their ability to transfer multiple electrons. Molten air batteries made with iron, carbon or vanadium boride can store three, four and 11 electrons per molecule respectively, giving them 20 to 50 times the storage capacity of a lithium-ion battery, which is only able to store one electron per molecule of lithium.

"Molten air introduces an entirely new class of batteries," Licht said.

Other multiple-electron-per-molecule batteries the Licht group has introduced, such as the super-iron or coated vanadium boride air battery, also have high storage capacities. But they had one serious drawback: They were not rechargeable. Rechargeable molten batteries (without air), such as a molten sulfur battery, have been previously investigated, but are limited by a low storage capacity.

The new molten air batteries, by contrast, offer the best of both worlds: a combination of high storage capacity and reversibility. As the name implies, air acts as one of the battery electrodes, while simple nickel or iron electrodes can serve as the other. "Molten" refers to the electrolyte, which is mixed with reactants for iron, carbon or vanadium boride, then heated until the mixture becomes liquid. The liquid electrolyte covers the metal electrode and is also exposed to the air electrode.

Researchers have created molten air batteries using iron, carbon and vanadium boride because of their ability to transfer multiple electrons. These batteries can store three, four and 11 electrons per molecule respectively, giving them 20 to 50 times the storage capacity of a lithium battery, which can only store one electron per molecule of lithium.

The batteries are able to recharge by electrochemically reinserting a large number of electrons. The rechargeable battery uses oxygen directly from the air, not stored, to yield high battery capacity. The high activity of molten electrolytes is what allows this charging to occur, according to Licht.

The electrolytes are all melted to a liquid by temperatures between 700 and 800 degrees Celsius. This high-temperature requirement is challenging to operate inside a vehicle, but such temperatures are also reached in conventional internal combustion engines.

A molten air battery configuration: The air electrode (circle, left) and the metal electrode (right) are lowered into the crucible (white cup), then covered with electrolyte, which is then heated until it is molten. Molten air batteries have the highest intrinsic electric energy storage capacities of any other batteries to date.

Credit: *William Atkins, the George Washington University*

The researchers continue to work on their model to make the batteries viable candidates for extending electric cars' driving range. In the Licht group's latest study, the molten air battery operating temperature has been lowered to 600 degrees Celsius or less. The new class of molten-air batteries could also be used for large-scale energy storage for electric grids.

"A high-temperature battery is unusual for a vehicle, but we know it has feasibility," Licht said. "It presents an interesting engineering question."

Molten-air battery's storage capacity among the highest of any battery type

Anode	Formula Weight kg mol^{-1}	e^-s stored	Charge Capacity Ah/kg	d, kg l^{-1}	E°, V vs O_2	Energy Capacity gravimetric Wh kg^{-1}	Energy Capacity volumetric Wh $liter^{-1}$
Iron	0.05585	$3e^-$	1,440	7.2	1.0	1,400	10,000
Carbon	0.01201	$4e^-$	8,930	2.1	1.0	8,900	19,000
VB_2	0.07256	$11e^-$	4,060	5.1	1.3	5,300	27,000

This chart compares the characteristics of molten-air batteries that use three different types of materials. Credit: Licht, et al. Â©2013 The Royal Society of Chemistry

(Phys.org) —Researchers have demonstrated a new class of high-energy battery, called a "molten-air battery," that has one of the highest storage capacities of any battery type to date. Unlike some other high-energy batteries, the molten-air battery has the advantage of being rechargeable. Although the molten electrolyte currently requires high-temperature operation, the battery is so new that the researchers hope that experimenting with different molten compositions and other characteristics will make molten-air batteries strong competitors in electric vehicles and for storing energy for the electric grid.

The researchers, Stuart Licht, Baochen Cui, Jessica Stuart, Baohui Wang, and Jason Lau, at George Washington University, have published a paper on the new molten-air battery in a recent issue of *Energy & Environmental Science*.

"This is the first time that a rechargeable molten-air battery has been demonstrated," Licht told *Phys.org*. "There have been rechargeable batteries that use molten electrolytes, but not air. For example, molten-sulfur batteries have been widely studied for electric car and grid applications. However, sulfur is twice as massive as oxygen (per electron stored) and its mass needs to be carried as part of the battery (whereas air is freely available). The molten-air batteries are the first rechargeable batteries to use a molten salt to store energy using 'free' oxygen from the air and multi-electron storage molecules."

This ability to store multiple electrons in a single molecule is one of the biggest advantages of the molten-air battery. By their nature, multiple-electron-per-molecule batteries usually have higher storage capacities compared to single-electron-per-molecule batteries, such as Li-ion batteries. The battery with the highest energy capacity to date, the vanadium boride (VB2)-air battery, can store 11 electrons per molecule. However, the VB2-air battery and many other high-capacity batteries have a serious drawback: they are not rechargeable.

Here, the researchers demonstrated that molten-air batteries offer a combination of high storage capacity and reversibility. The molten-air battery uses oxygen from the air as the cathode material, giving it the benefit of not having to carry this weight. It also has the advantage of not using any exotic catalysts or membranes. Different versions of the battery use different electrolytes, but they are all molten, i.e., melted to a liquid by a high temperature, in this case around 700-800 °C.

The researchers experimented with using iron, carbon, and VB2 as the molten electrolyte, demonstrating very high capacities of 10,000, 19,000, and 27,000 Wh/l, respectively. The capacities are influenced by the number of electrons that each type of molecule can store: 3 electrons for iron, 4 electrons for carbon, and 11 electrons for VB2. In comparison, the Li-air battery has an energy capacity of 6,200 Wh/l, due to its single-electron-per-molecule transfer and lower density than the other compositions.

The researchers explain that they were able to make the battery reversible by using an unusual electrolytic splitting process to function as battery "charging." For example, when the iron molten-air battery is discharged, the iron mixes with the oxygen to produce iron oxide. To charge the battery, the iron oxide is converted back into iron metal, and O2 is released into the air. The carbon and VB2 molten-air batteries recharge in a similar way, although the electrochemical properties of VB2 are not as well understood as the others.

As Licht explained, the molten electrolyte is a key to making the battery rechargeable.

"In the case of molten-air batteries, the molten electrolyte opens a pathway to recharge a wide variety of high-capacity multi-electron storage materials," he said. "These materials, while highest in capacity, are a challenge to recharge (how do you reinsert 11 electrons back into each molecule of vanadium boride?). The molten electrolyte provides an effective media that is compatible with both recharging these materials and 'free' oxygen from the air for storage. The high activity of molten electrolytes allows this charging to occur."

While the molten-air battery's high capacity and reversibility make it an attractive candidate for future energy storage applications, the researchers are continuing to improve other areas of the battery. For example, they plan to investigate other types of molten electrolytes with lower melting temperatures, increasing the voltage (a major contributor to power density and, for electric vehicles, maximum speed), and improving the energy efficiency.

"High temperature for a battery is unusual," Licht said. "However, it is not an impediment. Lower capacity, high-temperature molten electrolyte sulfur batteries have already been tested without incident in electric vehicles. No weak spot has yet appeared. The discharge current of the molten-air electrode is sufficient to yield high battery voltages, but as described in the study could be even greater when a higher surface area between the cycled air and the molten salt will be achieved."

More information: Stuart Licht, et al. "Molten Air – A new, highest energy class of rechargeable batteries." *Energy & Environmental Science*. DOI: 10.1039/C3EE42654H
Also at arXiv:1307.1305 [physics.chem-ph] http://arxiv.org/abs/1307.1305

Posted: Sep 16, 2013

A new class of high-energy rechargeable batteries - molten air

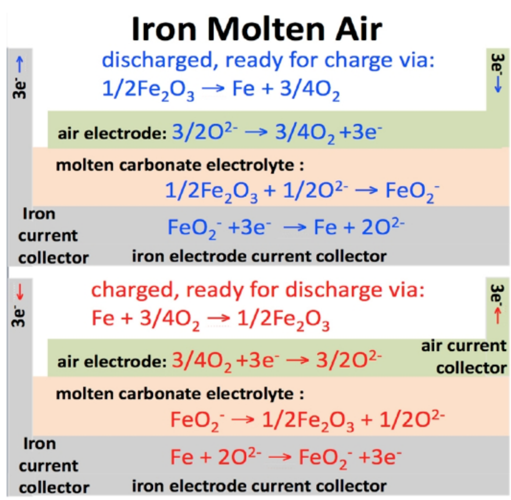
(*Nanowerk Spotlight*) Oxygen is an advantageous battery storage material as it is freely available from the air and does not need to be carried with the other battery components. Unlike the lithium-ion batteries used today, lithium–oxygen batteries do not require metal oxide cathodes to produce electrochemical power, instead generating power from reactions with oxygen in the atmosphere. Air has been widely used in single-use disposable batteries, such as hearing aid batteries. However, attempts to date to use air in rechargeable batteries has not led to viable systems.

For example, lithium-air batteries have recently been attempted by replacing the conventional Li-ion battery cathode with air (see for instance: "A nanoscale glimpse of batteries in action"). However, to date these lithium-air batteries have not met with success due to their need for non-reactive resistive electrolytes and the low density of lithium compounds which leads to a low volumetric battery capacity.

A new class of rechargeable batteries – 'molten air' batteries – solve these challenges by using highly conductive molten electrolytes and very high capacity multiple electron compounds such as carbon and vanadium diboride (VB2). Unlike prior rechargeable molten batteries, the molten air battery is not burdened by the weight of the active chargeable cathode material. The rechargeable molten air electrode instead uses oxygen directly from the air to yield high battery capacity.

"Molten air batteries advance the field of energy storage by opening up multiple opportunities for new higher capacity batteries," Stuart Licht, a professor of chemistry at George Washington University, tells Nanowerk. "These are the first batteries to reversibly use oxygen from the air to store energy via a molten salt and multiple electrons stored per molecule at the counter electrode."

In a new paper in the September 12, 2013 online edition of *Energy & Environmental Science* ("Molten Air - A new, highest energy class of rechargeable batteries"), Licht and his team establish the foundation, experimental demonstration, and proof of principle of a new class of molten air batteries.



Top: The molten air battery. Bottom: The iron molten air battery. The charging or discharging process is indicated by red or blue text & arrows. (Image: Stuart Licht, George Washington University)

In their work, the researchers demonstrate three working examples of the new battery's electron transfer chemistry. They include the energy stored in the battery by the 4 electrons released by carbon, the 3 electrons released by iron, and the 11 electrons released by vanadium diboride. These air battery examples have greater respective intrinsic volumetric energy capacities – 10,000 (for Fe to Fe(III)), 19,000 (C to CO_3^{2-}) and 27,000 Wh liter^{-1} (VB_2 to B_2O_3 + V_2O_5) – much higher than that of the lithium air battery at 6,200 Wh liter^{-1}.

This proof of concept study demonstrates the principles of the molten air battery class with three new batteries. Licht and his team expect there will be new demonstrations of other molten air batteries, chemical explorations of the energy storage mechanisms, and engineering optimization of the cell.

"The discharge current of the molten air electrode is sufficient to yield high battery voltages, but could be even greater when a higher surface area between the cycled air and the molten salt will be achieved," says Licht.

Potential applications of these molten air batteries could be large scale energy storage for electric grids (for example to store electricity when wind or solar electric is not available); higher storage capacity for electric cars (for example this system has much greater capacity than high temperature sodium sulfur batteries which had been previously investigated); or higher storage capacity for drones.

By Michael Berger.

Posted: May 26, 2014

Improved molten air battery operates at lower temperatures

(*Nanowerk Spotlight*) One of the biggest obstacles that is holding back the wide-spread adoption of electric cars is the insufficient performance of batteries. They don't last very long, requiring a very dense network of charging stations, they are heavy, and they are expensive.

A new class of high-density, rechargeable batteries might change this picture by addressing the 'range anxiety' that is inherent to current electric vehicles by drastically increasing their battery capacity: molten air batteries have up to 50 times the storage capacity of lithium-ion batteries. These batteries reversibly use oxygen from the air to store energy via a molten salt and multiple electrons stored per molecule at the counter electrode. We introduced this concept to our readers in a previous *Nanowerk Spotlight* ("A new class of high-energy rechargeable batteries - molten air").

Unlike previous rechargeable molten batteries, the molten air battery is not burdened by the weight of the active chargeable cathode material. The rechargeable molten air electrode instead uses oxygen directly from the air to yield high battery capacity.

"We start with iron, carbon or vanadium boride for their ability to transfer multiple electrons," Stuart Licht, a professor of chemistry at George Washington University, explains to Nanowerk. "Molten air batteries made with these materials can store three, four and 11 electrons per molecule respectively, giving them 20 to 50 times the storage capacity of a lithium-ion battery, which is only able to store a maximum of one electron per molecule of lithium."

Licht and his team have now published a new study in the May 2, 2014 online edition of *Journal of Materials Chemistry A* ("A Low Temperature Iron Molten Air Battery"), in which they introduce a more EV (electric vehicle) compatible, i.e. lower temperature, version of their molten air battery, and demonstrate this with one version – iron molten air – of the battery.

Various molten air battery chemistries. (Image: Licht Group, University of Washington)

Previous versions of the molten air battery operated at temperatures of 700°C to 800°C, which is about the same level that is typically reached by internal combustion engines driven by gasoline. The refined version of the iron molten air battery introduced in this paper can operate at a working temperatures below 600°C, which makes it more compatible with EV applications.

Licht notes that, in addition to electric vehicles, these molten air batteries have a high capacity and potential for low cost – they function with inexpensive steel and nickel electrodes – for electric grid storage applications. The storage of energy for the electric grid increases the viability of renewable energy to provide continuous electricity when sunlight or wind is not available.

"The battery design is scalable and we are interested in moving the battery from laboratory to larger prototypes," he concludes.

By Michael Berger. Copyright © Nanowerk

Green Car Congress

Energy, technologies, issues and policies for sustainable mobility

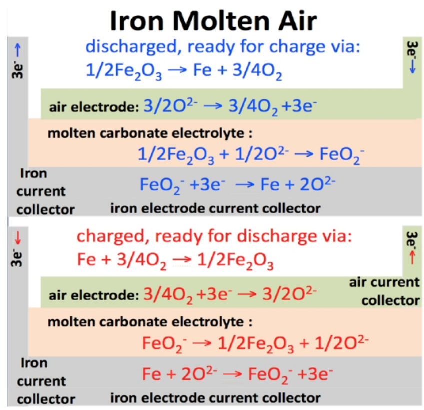
Researchers present lower temperature version of ultra-high capacity molten air battery

27 May 2014

Last year, researchers at George Washington University led by Dr. Stuart Licht introduced the principles of a new class rechargeable molten air batteries that offer amongst the highest intrinsic electric energy storage capabilities. (Earlier post.) The iron, carbon and VB_2 molten air batteries they proposed offered intrinsic volumetric energy capacities of 10,000 (for Fe to Fe(III)); 19,000 (C to CO_3^{2-}) and 27,000 Wh liter^{-1} (VB_2 to B_2O_3 + V_2O_5), compared to 6,200 Wh liter^{-1} for a lithium-air battery.

Now, in a new paper in the RSC's *Journal of Materials Chemistry A*, Baochen Cui and Licht report on a lower-temperature iron molten air battery that they suggest would be more compatible with electric vehicle applications.

A rechargeable molten air battery (MAB) uses an air cathode, a molten electrolyte and a high capacity multi-electron anode. Discharging MABs couple the cathodic reduction of O_2 (from the air) with anodic multi-electron/molecule oxidation to yield the high intrinsic storage capacities. As examples, the VB_2 MAB offers 11-electron oxidation; the carbon, 4-electron; and the iron, 3-electron.



The iron molten air battery; illustration of the charge/discharge in molten carbonate. The charging or discharging process is indicated by red or blue text & arrows. Cui and Licht,

In earlier work, the team demonstrated the Molten Air Battery chemistries at temperatures of 730 °C to 800 °C.

Unlike the challenges to study of the Carbon or VB_2 Molten Air Batteries by constraining their intrinsic capacity, the capacity of an Iron Molten Air Battery can be controlled by limiting the iron added to the cell. As one example of the recently introduced molten air battery class, we probe here the rechargeable nature of the Iron Molten Air Battery. Of the three examples of molten air batteries provided to date, the Iron Molten Air example provides the easiest route to purposely restrict the battery capacity by limiting the iron reactant (by allowing free flow entry of air, but by constraining the concentration of dissolved iron salt in the electrolyte). We will probe sustainable current densities and discharge efficacy, and then demonstrate a pathway to lower temperature rechargeable Iron Molten Air batteries.

—Cui and Licht, Supplementary Information

To achieve the lower temperature, the team moved from a lithium carbonate (Li_2CO_3) electrolyte which melts at 723 ˚C to the alkali carbonate eutectic (having the lowest melting point possible) $Li_{0.87}Na_{0.63}K_{0.50}CO_3$ which melts at around 393 ˚C.

The solubility of iron in the eutectic electrolyte is high, and at 750 °C approaches half the solubility of the high solubility in the pure lithium carbonate electrolyte. The eutectic has the advantage of a greater molten temperature range—extending several hundred degrees lower than the pure lithium system). Compared to pure lithium carbonate, the alternative molten media has the disadvantage of lower conductivity, but the advantage of even greater availability, and the wider operating temperature domain.

In the paper, Bao and Licht compared iron MABs with the $Li_{0.87}Na_{0.63}K_{0.50}CO_3$ electrolyte at 600 ˚C or less with a battery with the 730 °C Li_2CO_3 electrolyte.

High voltage efficiency and cycling is observed at 600 ˚C, but polarization is excessive at 395 ˚C. In contrast to the low temperature advantage the eutectic electrolyte has two challenges. Li_2CO_3 is more conductive than electrolytes containing Na_2CO_3 or K_2CO_3, and Li_2O is more stabilizing than Na_2O or K_2O in carbonates or chlorides. We hope to explore if a new $BaCO_3$ additive can offset the disadvantages.

—Cui and Licht

Resources

Baochen Cui and Stuart Licht (2014) "A Low Temperature Iron Molten Air Battery," *J. Mater. Chem. A*, Accepted Manuscript doi: 10.1039/C4TA01290A

C&EN
CHEMICAL & ENGINEERING NEWS
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Molten Electrolyte-Air Battery Debuts

Uncommon electrochemical reactions may lead to batteries with exceptionally high charge capacities

By Mitch Jacoby

Department: Science & Technology | Collection: Sustainability
News Channels: Materials SCENE
Keywords: battery, metal-air battery, molten electrolyte, lithium-ion battery

George Washington University chemists report a new class of battery that draws oxygen from the air and features a molten electrolyte, which far outstrip commercial lithium-ion batteries.

One factor impeding wide use of electric vehicles is their limited driving range per charge compared with the driving range per fill-up of petroleum-fueled vehicles. New types of batteries with exceptionally high charge capacities could give electric cars a needed boost. George Washington University chemists now report that a new class of battery that draws oxygen from the air and features a molten electrolyte may do the trick (*Energy Environ. Sci.* 2013, DOI: 10.1039/c3ee42654h). Stuart Licht, Baochen Cui, and coworkers studied three types of rechargeable molten electrolyte-air batteries with theoretical charge capacities that are roughly 1.5 to 4.5 times as high as the capacity of prototype lithium-air batteries, which far outstrip commercial lithium-ion batteries. One of the group's high-capacity batteries uses a molten carbonate electrolyte and draws oxygen from the air to convert iron to iron oxide. Recharging the battery reverses the reaction. The team also demonstrated high capacities in batteries based on two other reversible reactions: converting elemental carbon to CO_3^{2-} and VB_2 to B_2O_3 and V_2O_5. A range of parameters needs to be explored to optimize the battery cycling characteristics, the researchers say.

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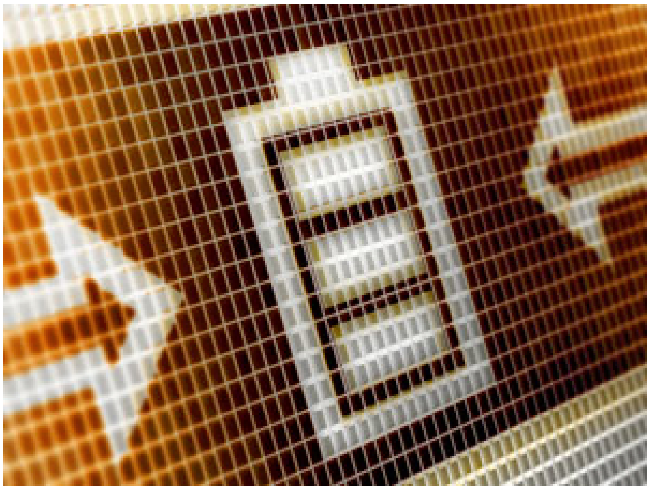
ROYAL SOCIETY OF CHEMISTRY

Molten air – a new class of battery

10 October 2013 Rowan Frame

Scientists from the US have invented a new type of battery. The so-called 'molten air batteries' have among the highest electrical storage capacities of all battery types to date.



The molten air batteries combine useful characteristics from existing types of batteries © Shutterstock

Inexpensive batteries with better energy storage densities are needed for many applications. For example, one barrier to the large-scale adoption of electric cars is the limited distance they can travel before their battery needs recharging.

Stuart Licht and his group at George Washington University think their molten air batteries could be the answer. They made three different versions of the battery using iron, carbon or vanadium boride as the molten electrolyte. Just like metal–air batteries, molten air batteries use oxygen from the air as the cathode material instead of an internal oxidiser, which makes them light. And similar to very high energy density vanadium boride–air batteries, molten air batteries can store many electrons per molecule.

Another important advantage of molten air batteries is that, unlike some other high energy batteries, the molten air battery is rechargeable. The high electrochemical activity of their molten electrolytes enables electrons to be stuffed back into the electron-storing material via unusual electrochemical pathways.

'The high storage capacity of these batteries is extraordinary to observe,' says Licht. He was also surprised by the stability of components made from steel and nickel foil in the diverse range of molten electrolytes.

'This is the first report of a rechargeable high temperature air battery,' says Derek Fray, a molten salts expert at the University of Cambridge in the UK. 'It will be fascinating to follow the technical development of this important innovation.'

The group are now working on understanding and optimising the science and engineering of the new molten air batteries and think that their work will encourage others to research alternative molten air battery chemistries. Licht is optimistic: 'the basic components – inorganic salts, nickel and steel – are readily available and inexpensive. Depending on the rate of scale-up, we might see molten air batteries used two years from now.'

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Friday 06 June 2014 - The Chemical Engineer

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Molten air batteries have the highest energy capacity of any battery

Lower temperature molten air battery made

More suitable for electric vehicles

Helen Tunnicliffe

30/05/2014

RESEARCHERS at George Washington University, US, have succeeded in lowering the operating temperature of molten air batteries, which have the highest energy capacity of any battery yet developed.

The new iron molten air battery works at temperatures below 600°C, which the researchers, Stuart Licht and Baochen Cui, say potentially make it suitable for use in electric vehicles, compared to around 800°C for previous molten air batteries. Licht and Cui announced that they had developed the first proof-of-concept molten air battery last September, consisting of a metal-based anode, with oxygen from air acting as the cathode, and a molten salt electrolyte. The best-performing, which contains vanadium boride (VB_2), has an energy capacity of 27,000 Wh/l. This is orders of magnitude higher than a standard lithium ion battery, which has a capacity of 600 Wh/l.

The anode in the new battery is made from iron. During use, the iron reacts with the oxygen in the air to form iron oxide. As the battery is recharged, the iron oxide dissolved in the electrolyte is converted back into iron metal at the electrode. The electrolyte is a salt made up of lithium, sodium, potassium and carbonate ions – $Li_{0.87}Na_{0.63}\,K_{0.50}CO_3$. This is eutectic, which means it melts at a lower temperature than the individual components.

The iron molten air battery has an energy capacity of 10,000 Wh/l. This high capacity of the battery is due to the very high solubility of Fe (III) ions in carbonates containing lithium ions. The battery is rechargeable with 92% efficiency.

Journal of Materials Chemistry A DOI: 10.1039/C4TA01290A

Green Car Congress

Energy, technologies, issues and policies for sustainable mobility

GWU researchers introduce new class of molten air batteries; significantly greater energy capacity than Li-air

13 September 2013

Generalized form of the molten air battery. Licht et al. Click to enlarge.

Researchers at George Washington University led by Dr. Stuart Licht have introduced the principles of a new class rechargeable molten air batteries that offer amongst the highest intrinsic electric energy storage capabilities.

In a paper just accepted and published online by the RSC journal *Energy & Environmental Science*, Licht and his colleagues show three examples of the new battery's electron transfer chemistry. These are the iron, carbon and VB_2 molten air batteries with respective intrinsic volumetric energy capacities of 10,000 (for Fe to Fe(III)); 19,000 (C to CO_3^{2-}) and 27,000 Wh liter^{-1} (VB_2 to B_2O_3 + V_2O_5), compared to 6,200 Wh liter^{-1} for the lithium-air battery.

> *In 2008 a zirconia stabilized VB_2 air battery was presented. [Earlier post.] This 11^{e-} (eleven electron) per molecule, room temperature, aqueous electrolyte battery has the highest volumetric energy capacity for a battery, with an intrinsic capacity greater than that of gasoline and an order of magnitude higher than that of conventional lithium ion batteries. The challenge has been to recharge the battery; that is to electrochemically reinsert 11^{e-} into the battery discharge products. Here, this challenge is resolved through the introduction of a new class of molten air batteries.*
>
> *...Unlike prior rechargeable molten batteries, the [molten air] battery is not burdened by the weight of the active chargeable cathode material. The rechargeable molten air electrode instead uses oxygen directly from the air to yield high battery capacity. This electrode will be shown to be compatible with several high capacity multiple electron redox couples. Three demonstrated new batteries chemistries are the metal (iron), carbon and VB_2 molten air batteries with intrinsic volumetric energy capacities greater than that of the well known lithium air battery due to the latter's single electron transfer and low density limits.*
>
> —Licht *et al.*

As an example of the process, during the charging of the iron molten battery, iron oxide is converted to iron metal via a three-electron reduction, and oxygen is released to the air. During discharge, iron metal is converted back to iron oxide. Li_2CO_3, which melts at 723°C, and lower melting carbonate eutectics are effective electrolytes, the researchers found. Simple steel foil cathodes and nickel foil anodes are effective for either iron oxide or carbon dioxide splitting.

> *Iron has been widely explored for battery storage due to its availability as a resource and its capability for multiple electron charge transfer. Retention of the intrinsic anodic storage capacity of these batteries has been an ongoing challenge...In 2010 we introduced the molten carbonate electrolytic conversion of iron oxide to iron as a CO_2-free synthesis alternative to the conventional greenhouse gas intensive industrial production of iron metal. The unexpected, high solubility of iron oxide in lithiated molten carbonate electrolytes was demonstrated to lead to the facile splitting of iron oxide to iron metal with the concurrent release of oxygen.*
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> *Here, we consider this unusual electrolytic splitting as a battery "charging". We couple this with the known primary discharge of the air cathode as used in the widely studied molten carbonate fuel cell, including those using coal as a fuel, to explore the first example of a molten air rechargeable battery. In lieu of iron we also explore the alternative use of carbon and VB_2 as alternative high capacity discharge redox couples for these rechargeable cells.*
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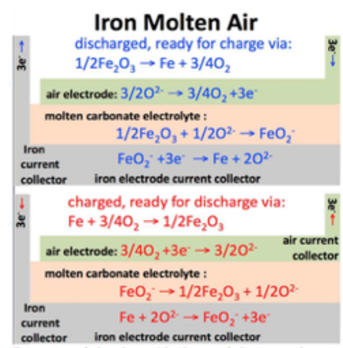


Illustration of the charge/discharge of the iron molten air battery in molten carbonate. The charging or discharging process is indicated by red or blue text & arrows. Licht et al. Click to enlarge.

For the carbon molten air battery, carbon formation during molten carbonate electrolysis provides the "charging"; molten carbonate cells have been widely probed as robust fuel cells. The combination of these two processes form the basis for the carbon molten air battery.

On the other hand, the researchers note, the foundation of understanding of the electrochemical VB_2 molten air system "*is small; there is little or no prior information pertaining to an electrochemical path for recharge of the molten vanadate (V_2O_5) and molten borate (B_2O_3) discharge products*".

The studies reported in the paper are less advanced that with the other two chemistries due to the scarcity of prior fundamental electrochemical knowledge of the molten system.

Advancing the new class of molten air batteries will require the exploration of an extensive range of parameters such as electrolyte and gas composition; electrode morphology; temperature; and cycle rates, the authors point out.

> *For example, while these experiments have been conducted in the 700 °C to 800 °C temperature range, the molten carbonate electrolyte has a wide range of electrolyte opportunities, such as through the use of mixed alkali carbonate eutectics which exhibit a minimum melting point below 400 °C. Enhancements of the morphology and modifications of the electrocatalytic nature of the air electrode should improve energy efficiency of the cell. A range of cell configurations with lower polarization (with similar discharge potentials, but supporting significantly higher current density) will be reported in a future study.*
>
> —Licht *et al.*

Resources

- Stuart Licht, Baochen Cui, Jessica Stuart, Baohui Wang and Jason Lau (2013) Molten Air - A new, highest energy class of rechargeable batteries. *Energy Environ. Sci.* doi: 10.1039/C3EE42654H

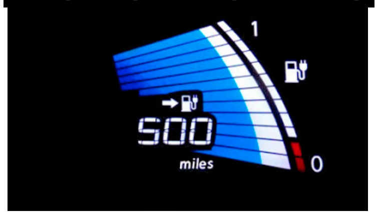
Molten Air Press reports

autoevolution

Molten-Air Batteries Might Give EVs 7,000 Miles Range

at: autoevolution.com/news/molten-air-batteries-might-give-evs-7000-miles-range-83399.html

ELECTRIC VEHICLE NEWS



Molten-air battery offers up to 45x higher storage capacity than Li-ion

FRIDAY, SEPTEMBER 20, 2103

at: electric-vehiclenews.com/2013/09/molten-air-battery-offers-up-to-45x.html

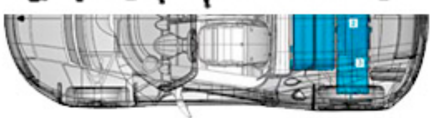
Electromotive News | Electric Car News

WILL MOLTEN-AIR BATTERY TECHNOLOGY SPARK YOUR INTEREST?

OCTOBER 11, 2013

at: electromotivenews.com/will-molten-air-battery-technology-spark-interest

InsideEVs



New Type of Molten Air Battery Promises Energy Capacity Way Beyond Even Lithium Air

by Eric Loveday

at: insideevs.com/new-type-of-molten-air-battery-promises-energy-capacity-way-beyond-even-lithium-air

EV WORLD.COM

Study Investigates Potential of Molten Air Battery

Molten air would have even greater energy storage capacity than lithium air with potential application in renewable energy storage, electric vehicles and UAVs.

Published: 16-Sep-2013

at: evworld.com/news.cfm?newsid=31270

TechnoDuet

Molten Air Battery – A Hot One for a Long Ride

BY TARIQUE HAIDER · SEPTEMBER 24, 2013

at: technoduet.com/molten-air-battery-a-hot-one-for-a-long-ride

eCarTec

Researchers present lower temperature version of ultra-high capacity molten air battery

02. June 2014

at:ecartec.de/en/news/?tx_ttnews%5Btt_news%5D=1640&cHash=b19f756840e73b8bbdab0c4f768bdda5

The Green Optimistic

Electric Vehicle Range Could Expand with New Rechargeable Molten-Air Battery

Benji Jerew July 2, 2014

at: greenoptimistic.com/2014/07/02/electric-vehicle-range-expand-new-rechargeable-molten-air-battery/#.U8A0bCikK6h

New Molten-air Battery Has the Highest Storage Capacity Ever Seen

Mila Luleva September 20, 2013

at: greenoptimistic.com/2013/09/20/new-rechargeable-molten-air-battery-highest-storage-capacity/#.U8A0QSikK6h

EVBud.com

7/1/14 3:44 pm chumakdenis

Molten-air battery

Molten-air battery offers up to 50x higher storage capacity than Li-ion

at: evbud.com/news/201

DECCAN Chronicle

New rechargeable batteries for electric vehicles developed

PTI | July 06, 2014, 14.07 pm IST

at: deccanchronicle.com/140706/technology-science-and-trends/article/new-rechargeable-batteries-electric-vehicles-developed

BMZ THE INNOVATION GROUP

NEW 06/30/14

Researchers present lower temperature version of ultra-high capacity molten air battery

at: bmz-gmbh.de/news/newsletter/0,2,5345,535.html

AutoB

Νέα τεχνολογία μπαταριών, μπορεί να δώσει αυτονομία της τάξης των 11.000+ χιλιομέτρων

Γράφει: Αλέξανδρος Αϊβάζογλου - 5 Ιουλίου 2014 , 14:30

at: autoblog.gr/2014/07/05/new-battery-technology-might-give-evs-11000-kilometers-range

QS ARTICLE

Engineering, Technology, Project Management

Molten Air | Molten Air Battery | Molten Air a New Class of Battery

January 6, 2014

at: qsarticle.com/molten-air-molten-air-battery-molten-air-a-new-class-of-battery

india.com ZeeNews

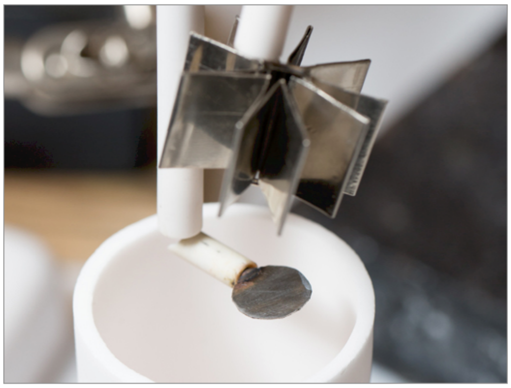
New high-energy rechargeable batteries developed

July 06, 2014,

at: zeenews.india.com/news/science/new-high-energy-rechargeable-batteries-developed_945482.html science360

06.30.14 News | Today's News

Molten air battery



With support from the National Science Foundation, researchers at George Washington University have created molten air batteries. The scientists used iron, carbon and vanadium boride because of their ability to transfer multiple electrons. These batteries can store three, four and 11 electrons per molecule respectively, giving them 20 to 50 times the storage capacity of a lithium battery, which can only store one electron per molecule of lithium. Pictured here is a molten air battery configuration: The air electrode (circle, left) and the metal electrode (right) are lowered into the crucible (white cup), then covered with electrolyte, which is then heated until it is molten.

at: news.science360.gov/obj/pic-day/cd57d049-a42d-4932-91a4-92d81ba6c329/molten-air-battery

Crazy Engineers

Molten air battery offers highest energy storage capacity & is rechargeable

by Kaustubh Katdare, Sep 22, 2013.

at: crazyengineers.com/threads/molten-air-battery-offers-highest-energy-storage-capacity-is-rechargeable.70817

Revolution-Green
Breakthrough Energy News

New Molten Air Battery Has Highest Capacity Yet

Batteries - Storage, Clean Energy, September 2013

at: revolution-green.com/new-molten-air-battery-highest-capacity-yet

Energy Storage World Forum

Molten Air – A New Class of High-Energy Rechargeable Batteries

at: energystorageforum.com/europe/news/molten-air-class-high-energy-rechargeable-batteries

Energy & Utilities

Energy & Utilities Network

Molten Air - A new, highest energy class of rechargeable batteries with up to 4.5 times the energy capacity of lithium air batteries [Analysis]

Jeffrey M D.
President at Thermoeconomics

at: linkedin.com/groups/Molten-Air-new-highest-energy-67258.S.275705999

Next Big Future

MOLTEN AIR - A NEW, HIGHEST ENERGY CLASS OF RECHARGEABLE BATTERIES WITH UP TO 45 TIMES THE ENERGY CAPACITY OF LITHIUM AIR BATTERIES

SEPTEMBER 21, 2013

at: nextbigfuture.com/2013/09/molten-air-new-highest-energy-class-of.html

the daily fusion

High-Capacity Molten Air Battery Developed

June 30, 2014

at: dailyfusion.net/2014/06/molten-air-battery-29821

Venice-MarVista Patch

New batteries are the highest capacity Molten air batteries for cars, grid balancing

by allen william , September 26, 2013

at: venice.patch.com/groups/allenwilliam/p/new-batteries-are-the-highest-capacity-molten-air-batteries-for-cars-grid-balancing

redOrbit
YOUR UNIVERSE ONLINE

Researchers Develop New, High-Energy Rechargeable Batteries

June 30, 2014

at: redorbit.com/news/science/1113181328/high-energy-rechargeable-batteries-developed-063014/

The Data Centre

Molten Air Batteries: High Storage Capacity but High Costs as Well

MONDAY, 30 SEPTEMBER 2013

at: blog.datacentre.me/2013/09/molten-air-batteries-high-storage.html

THE TIMES OF INDIA

Higher storage batteries developed

PTI | Jul 7, 2014, 04.18AM IST

at: timesofindia.indiatimes.com/home/science/Higher-storage-batteries-developed/articleshow/37929188.cms

Prezi

Molten Air batteries

by Mac Kelleher on 8 December 2013

at: prezi.com/lk4_rzsowtz8/copy-of-molten-air-batteries

Business Standard

New high-energy rechargeable batteries developed

Washington July 6, 2014

at: business-standard.com/article/pti-stories/new-high-energy-rechargeable-batteries-developed-114070600282_1.html

Qmed
QUALIFIED Suppliers to the Medical Device Industry

Could Molten Air Nanotechnology Power Future Medical Devices?

September 16, 2013

at: qmed.com/news/could-molten-air-nanotechnology-power-future-medical-devices?page=2

Chemical Technology

Chemical technology news from across RSC Publishing.

Driving power for electric cars

21 July 2008

Scientists have made the first renewable fuel cell that can store more energy than petrol.

Electric vehicles are potentially more environmentally friendly than petrol vehicles because they do not emit greenhouse gases, but the cells they use for power can't store as much energy as fossil fuels. Now, Stuart Licht and colleagues, have developed a vanadium boride-air fuel cell with a much larger energy capacity than current vehicle batteries. 'The cell has ten times the energy capacity of lithium ion batteries and three times the energy density of zinc-air batteries,' says Licht, 'although all these devices work in the same way.'

General Motors' electric car 'Volt'

In its electric car 'Volt', launching in 2010, General Motors (GM) uses a lithium ion battery which can power the car for 40 miles before it needs to be recharged. To extend this range, GM added a standard combustion engine to recharge the battery when it runs low.

> **"Our renewable fuel cell opens the door to electric vehicles with viable driving ranges, without a separate combustion engine and frequent battery recharges"- Stuart Licht**

The vanadium boride-air fuel cell needs only air and fresh fuel to complete the recharge process. Using this system, a motorist would drive into a fuel station, receive fresh fuel and drive away.

Peter Bruce, an expert in new materials for energy storage devices at St Andrews University, UK, comments: 'Finding ways to store more energy than is possible at present is a key challenge and imaginative solutions are necessary. Replacing the zinc in a zinc-air primary battery with a vanadium boride anode is certainly interesting. However, it does raise a number of challenges for practical devices, such as recharging the batteries, and more scientific questions to be answered.'

Licht acknowledges that there is lots of work to do before the fuel cell can be commercialised. 'This is a first study demonstrating the very high capacity of the cell. Engineering details, systems optimisation and scale-up need to be developed,' he says.

Janet Crombie

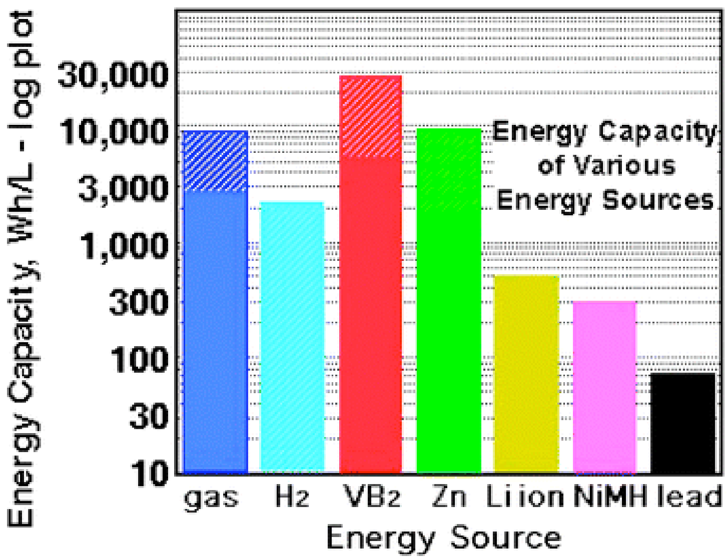
Link to journal article: Renewable highest capacity VB2/air energy storage
Stuart Licht, Huiming Wu, Xingwen Yu and Yufei Wang, Chem. Commun., 2008, 3257
DOI: 10.1039/b807929c

AL FIN ENERGY

http://alfin2300.blogspot.com/

JULY 25, 2008

New Battery Type Has More Energy Density



This new type of battery does not burn fuel like a fuel cell, and is not a reversible reaction like rechargeable batteries. But it does have comparable energy density to gasoline--a first for an electric battery type.

> *As in a zinc air cell, the vanadium boride cell reacts oxygen brought in via the cathode with the anode to produce electricity. And also as in a zinc-air cell, the reaction is irreversible;* ***spent anodes need to be replaced in a "refueling" operation and chemically regenerated****. (Earlier post.) The vanadium boride cells combine a conventional air cathode with a zirconia-stabilized vanadium boride anode.*

...For regeneration of the anodes, Licht and his team proposed a solar photochemical pathway based on Mg reduction of the fuel cell discharge products.

The large volumetric capacity of the fuel cell, and the pathway for a renewable (solar) energy recharge, are positive attributes of this novel vanadium boride air cell*. Systems aspects will continue to be analyzed and optimized. Liquid (higher temperature, solar driven), rather than solid, Mg, should facilitate the recharge formation of VB2...The discharge studies indicate that sub micron particle size VB2, as available following high energy ball milling, can further improve anodic kinetics and coulombic efficiency.*
—Licht 2008 _GCC

Achieving this level of energy density makes it worthwhile to explore efficient methods of recharging the cell. If the researchers can achieve a type of solar re-charging system, the new cell might form the basis of new electric vehicle fleets with ready access to a maintenance/recharge facility--taxis, buses, delivery vans, etc. Eventually it may be possible to achieve affordable and reliable home recharge for this type of cell.

Green Car Congress

Researchers Develop Vanadium Boride Air Cell; Twice the Practical Energy Capacity of Gasoline

25 July 2008

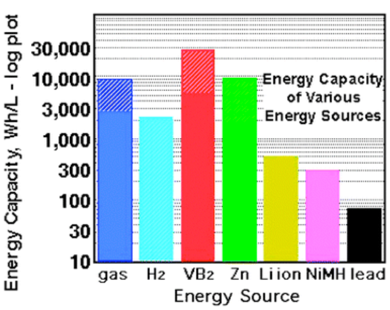
A team of researchers led by Dr. Stuart, has developed a vanadium boride (VB2)/air cell—a new renewable electrochemical energy system which stores more energy than gasoline and has an order of magnitude higher capacity than lithium-ion batteries. A report on their work is published in the 28 July issue of the journal Chemical Communications.

The energy capacity gap between gasoline and electrochemical storage systems has been a fundamental barrier to more widespread use of electric drive vehicles. Gasoline has a practical energy storage capacity of about 2.7 kWh/Liter, Li-ion about 0.5 kWh/L. Zinc-air cells, another high-capacity electrochemical system, have a practical capacity of about 1.75 Wh/L according to Licht and his colleagues. The new VB2 system has a practical capacity of 5 kWh/L, they calculate.

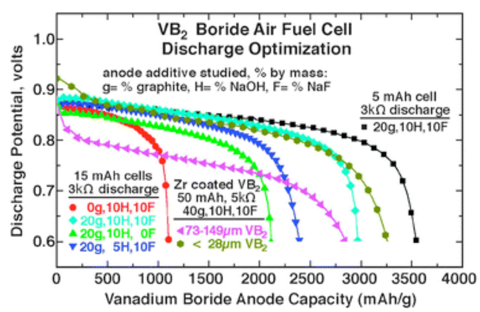
> Practical, compared to intrinsic, energy electrochemical capacity is limited by the delivered energy and system mass, incorporates all voltage losses, air cathode size, and all other cell components. For example, the practical energy of a small, portable commercial zinc air cell exceeds 18% of the intrinsic energy capacity, and can be higher in an optimized, large fuel cell configuration. The relative practical capacity of the VB2/air cell can be estimated as similar to that of the well studied Zn/air system (electrolytes and cathodes are similar). Based on this analog, the practical vanadium boride fuel has a lower limit of 18% of its intrinsic 27 kWh L-1, for an estimated vanadium boride air practical storage capacity of 5 kWh L-1.

—Licht 2008

As in a zinc air cell, the vanadium boride cell reacts oxygen brought in via the cathode with the anode to produce electricity. And also as in a zinc-air cell, the reaction is irreversible; spent anodes need to be replaced in a “refueling” operation and chemically regenerated. (Earlier post.) The vanadium boride cells combine a conventional air cathode with a zirconia-stabilized vanadium boride anode.



Energy capacity comparison of gasoline, hydrogen and electrochemical energy sources. Shading superimposed on solid colors indicates practical capacities.



Optimization of the vanadium boride air cell anode capacity as a function of the indicated anode composition, capacity, and discharge load conditions. Click to enlarge. Source: Licht 2008.

The researchers used the zirconia coating to avoid issues such as boride corrosion, which can result in “not only a chemical loss of the electrochemical capacity, but evolved hydrogen is flammable, and the evolved gas can swell or even crack a cell.” Zirconia is highly stable and maintains effective charge transfer during boride anodic discharge.

The researchers overcame a series of impediments to the effective discharge of the vanadium boride fuel cell and showed experimentally that they could realize substantial capacity of VB2. (See plot at right.)

For regeneration of the anodes, Licht and his team proposed a solar photochemical pathway based on Mg reduction of the fuel cell discharge products.

> The large volumetric capacity of the fuel cell, and the pathway for a renewable (solar) energy recharge, are positive attributes of this novel vanadium boride air cell. Systems aspects will continue to be analyzed and optimized. Liquid (higher temperature, solar driven), rather than solid, Mg, should facilitate the recharge formation of VB2...The discharge studies indicate that sub micron particle size VB2, as available following high energy ball milling, can further improve anodic kinetics and coulombic efficiency.

—Licht 2008

This material was based on work supported in part by the United States National Science Foundation, with research support to Stuart Licht while working at the Foundation.

Resources

Stuart Licht, Huiming Wu, Xingwen Yu and Yufei Wang (2008) Renewable highest capacity VB2/air energy storage. Chem. Commun., 2008, 3257-3259 doi: 10.1039/b807929c

The scientific article on the vanadium boride fuel cell is attached.
Other popular press descriptions of this
fuel with higher capacity than gasoline are titled:

Yahoo! News

New 'fuel battery' may ditch gasoline for good

Sat, Jul 26

The Economic Times

New fuel battery may ditch gasoline for good

26 Jul, 2008

The Daily Reckoning

Battery with 2X energy density of gasoline

Researchers Develop Vanadium Boride Air Cell; Twice the Practical Energy Capacity of Gasoline
25 July 2008

The Chemical Engineer 28/7/2008

Vanadium boride bears fuel cell hopes

New technology promises twice the capacity of petrol

by Claudia Flavell-While

Developing better fuel cells for car is a critical task

New Scientist

NewScientistTech

'Fuel battery' could take cars beyond petrol

25 July 2008 Colin Barras

Latest Car News

The New Hybrid - Fuel Systems and Batteries Combined

July 29th, 2008

New fuel-battery combines batteries with fuel system and could overtake the gasoline fuel source.

SCIENCE NEWS
THE WEEKLY NEWSMAGAZINE OF SCIENCE

Iron Power: Eking more juice from batteries

Many of the rechargeable batteries that power cell phones, laptop computers, medical implants, and hybrid cars contain some of the same electrode technology that was used in Thomas Edison's day. Now, chemists have come up with a modern alternative that could potentially multiply the capacity of such batteries.

A battery typically consists of two electrodes—a positive cathode and a negative anode—immersed in a substance through which charged atoms, or ions, can flow. The new technology holds promise for replacing the energy-limiting nickel-based cathode in nickel-metal hydride batteries, says chemist Stuart Licht of the University of Massachusetts in Boston, who led the research. Those are the most popular rechargeable batteries for portable electronic gadgets.

Whether powering a gadget or a car, nickel ions in the cathodes of such batteries each capture one electron arriving from the anode. By contrast, the new cathode employs salts of an unusual ionic form of iron—hexavalent or superoxidized iron—that readily accept three electrons per ion, Licht explains. The more electrons the cathode can accept, the more electricity the battery can supply.

Using superoxidized iron in a cathode isn't new. Licht and his coworkers achieved that milestone in 1999 (*SN: 8/28/99, p. 141*). However, the researchers relied on iron-salt crystals the size of fine sand grains, and the prototype batteries made with these materials weren't rechargeable.

Licht and Ran Tel-Vered of the Technion Israel Institute of Technology in Haifa have turned to electrochemical-processing techniques to make grains roughly a billionth the volume of previous ones. With these smaller grains, the scientists created a cathode so thin that incoming electrons can find their way to virtually all of the cathode's ions. Because of that same nanoscale thinness, the electrode can be charged and discharged 200 times, the scientists report in the current issue of *Chemical Communications*.

Although that's less than half the minimum number of recharging cycles expected from a commercial battery, the new work shows that there's no fundamental barrier to designing rechargeable batteries with superoxidized iron, Licht says.

"Iron has possibilities," comments Stanford R. Ovshinsky of the company Energy Conversion Devices in Rochester Hills, Mich. Still, the new technology is "far from being a useful battery," notes Ovshinsky, who invented the metal hydride battery about 20 years ago.

"What [Licht] has done is extremely encouraging," says Digby D. Macdonald of Pennsylvania State University in State College. While the new cathode technology is still at an early stage, he adds, "it's certainly one of the most promising cathodes around." —P. WEISS

Technion Embraces the Future
TECHNION
FOCUS
INTERNET: http://www.technion.ac.il
Technion – Israel Institute of Technology, Division of Public Affairs & Resource Development, September/October 1999

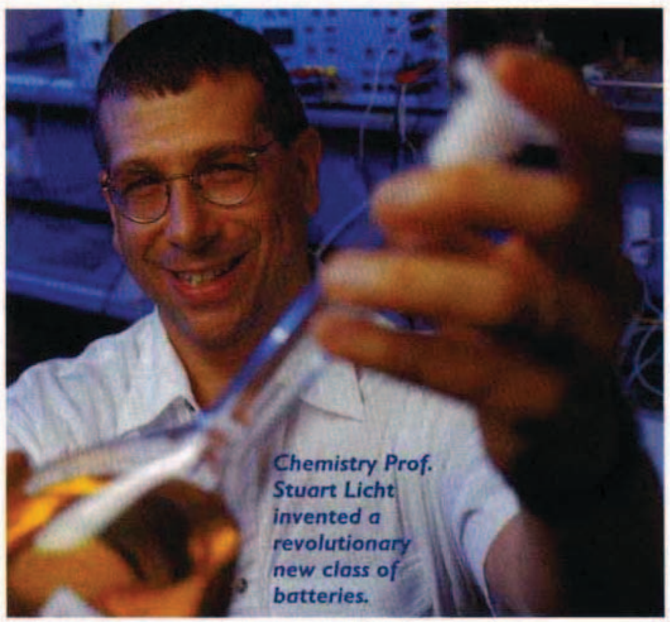
BETTER BATTERIES

New "Super-Iron" Batteries are Cleaner, Stronger and Longer Lasting

More than a century after Italian physicist Alessandro Volta invented the first electric battery, a Technion professor has discovered a revolutionary new class of batteries that may render conventional batteries obsolete.

Prof. Stuart Licht of the Faculty of Chemistry is attracting worldwide attention for his breakthrough discovery of "super-iron" batteries, the first significant improvement in battery technology since alkaline batteries were invented in 1860. Licht's patented batteries not only last considerably longer than conventional models, they also contain fewer toxic metals, making them environmentally safer when thrown away.

The new batteries are rechargeable and can be used anywhere from portable CD players to medical implants. According to Licht's report in the Aug. 13 issue of *Science*, super-iron batteries have more than 50 percent energy advantage compared to conventional alkaline batteries, and provide a 200 percent higher energy capacity increase in terms of high-drain rate. Licht defined high-drain rate as the rapid use of the electrical energy stored in the battery such as in cameras, portable CD players and cellular phones. "For example, a conventional AAA size alkaline battery may last only a few minutes at high drain rate, but under the same conditions an AAA super-iron battery discharges for well over an hour," said Licht.



Chemistry Prof. Stuart Licht invented a revolutionary new class of batteries.

The professor's research into the subject was sparked by a desire to reduce wasteful disposal in electronics. An estimated 60 billion primary batteries are consumed each year, which amounts to roughly 10 batteries for every human being on earth. "I enjoy today's high-tech gadgets as much as anyone, yet they are wasteful of batteries," he said. "I was specifically searching for materials to cut down on this wasteful disposal – materials that are compatible with existing battery systems, and that are environmentally 'clean'."

Licht reports that no researcher had attempted to use super-iron in a battery for generations because it rusts so easily. "We found we are able to stabilize the batteries in the caustic solution commonly used in today's primary and metal hydride batteries," Licht said. "The caustic solutions not only stop the super-iron from decomposing, but are basically the same as that used in alkaline batteries and therefore excellent for electrical energy storage." Nearly all of the primary batteries used each year are dry or alkaline batteries, he added. Both types use manganese dioxide and zinc.

"It is always the dream of the inventor to see his invention come to fruition and be useful to society." Prof. Stuart Licht

"The new battery replaces its heaviest portion (which is manganese dioxide) with a very unusual material, super-iron, which has a much higher electrical energy storage," Licht said.

Batteries use chemical reactions to convert chemical energy from metals at its two electrodes, the positive cathode and the negative anode, into electrical energy. A battery dies when the metals at either electrode are used up. Licht's super-iron is ferrate, an unusual form of iron combined with oxygen. It is usually unstable but he found that if it is kept very pure, it stays in a stable and usable form.

The batteries release no toxic chemicals into the environment, unlike alkaline batteries, Licht said. "The super-iron cathode eventually turns into environmentally 'green' iron rust, which is preferable to the often poisonous compounds in many of the batteries presently used," he said.

DISCOVER MAGAZINE AWARDS
FOR TECHNOLOGICAL INNOVATION

Super Iron Battery Technology

Stuart Licht

July 1, 2000

In celebration of the spirit of curiosity and ingenuity that leads to technological innovation, Discover Magazine is proud to recognize those men and women who are working to improve our world.

Stephen L. Petranek
Editor in Chief
Discover Magazine

INDUSTRYWEEK
IW
THE MANAGEMENT RESOURCE

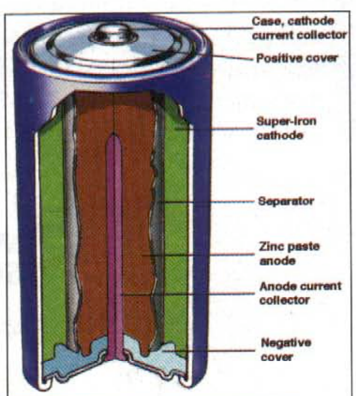
Technion-Israel Institute of Technology

Haifa, Israel

Super-Iron Battery

The Israel Institute of Technology's new Super-Iron Battery seems poised to hit the new-product trifecta.

First, consumers with portable, power-hungry electronic devices will profit because it lasts 50% longer than traditional batteries and 200% longer in high-drain applications. Second, it will please technology-wary environmentalists because it contains fewer toxic metals than traditional batteries and its super-iron cathode degenerates into environmentally friendly rust. And third, it will satisfy bottom-liners because the super-iron cathode is made from common, inexpensive materials—iron is the second-most predominant metal on earth—and the battery can be manufactured in the rechargeable forms needed for a variety of hot products including laptops, camcorders, and electric cars.



Technion: *Super-Iron Battery*

Still in the development stage, the super-iron battery looks like a traditional battery on the outside. The difference is within, where the Israeli scientists have changed a design used since the 19th century. "Nearly all of the approximately 60 billion primary batteries used each year are either dry or alkaline," explains Stuart Licht, the chemistry professor who led the research team. "Alkaline and dry batteries all use the same two active electrical-storage ingredients—manganese dioxide and zinc. The new super-iron battery replaces the heaviest portion, the manganese dioxide, with super iron, which has a much higher electrical-energy storage."

Licht says that most scientists are unfamiliar with super iron and that other researchers had concluded that it was too unstable for batteries. However, he and his team discovered that the caustic solutions commonly used in traditional batteries actually stabilize the super iron, making it the perfect material for these next-generation batteries.

Newsweek

THE INTERNATIONAL NEWSMAGAZINE
September 6, 1999

TECHNOLOGY

Do Not Store With Kryptonite

ADDICTED TO PORTABLE electronics but hate adding to the 60 billion or so alkaline batteries that get tossed every year? New research from Israel may help ease the guilt. By replacing the standard manganese cathode with a compound called "super-iron," Stuart Licht and his team squeezed up to 200 percent more energy from AAA-type cells. Super-iron can also boost the output of rechargeables and watch batteries, the researchers say. And when the stuff finally does end up in the landfill, it breaks down into harmless rust.

ESTHER PAN, THOMAS HAYDEN *and* WALAIKA HASKINS

page 10

The New York Times

Science Times

F1

TUESDAY, AUGUST 17, 1999

The New York Times

More Power, Less Poison in a Battery

WASHINGTON, Aug. 16 (Reuters) — A new iron-based battery not only lasts much longer than conventional batteries, Israeli researchers say, but contains fewer toxic metals and is gentler to the environment when thrown away.

The new "super-iron" batteries are rechargeable and can be used in anything from portable compact disk players to medical implants, the researchers wrote in the journal Science last week.

The batteries have a particular advantage in appliances with a high drain on electrical energy, like cameras, portable CD players and cellular phones.

"A conventional AAA-size alkaline battery may last only a few minutes at high drain rate," said the lead researcher, Stuart Licht of the Technion-Israel Institute of Technology in Haifa, "but under the same conditions an AAA super-iron battery discharges for well over an hour."

Batteries use chemical reactions to convert energy from metals at two electrodes, the positive cathode and the negative anode, into electricity. A battery dies when the metals at either electrode are used up.

The Israeli team's super-iron is ferrate, an unusual form of iron combined with oxygen. It is usually unstable, but the researchers found that if it was kept very pure, it stayed in a stable form.

The batteries, which use either potassium ferrate or barium ferrate cathodes, release no toxic chemicals into the environment, Mr. Licht said, adding, "The super-iron cathode eventually turns into environmentally 'green' iron rust, which is preferable over the often poisonous compounds, varying from mercury, cadmium, manganese and nickel oxides, that remain in many of the batteries presently used."

Mr. Licht said he had been searching for a battery that lasted longer and worked better than standard batteries.

"I enjoy today's high-tech gadgets as much as anyone, yet they are wasteful of batteries," he wrote in an E-mail interview. "I was specifically searching for materials to cut down on this wasteful disposal, compatible with existing battery systems, and which are environmentally 'clean' materials."

The alkaline battery was invented in 1860. But for generations, Mr. Licht said, no one had tried to use iron in batteries because it rusted so easily.

"We found we are able to stabilize them in the caustic solution commonly used in today's primary and metal-hydride batteries," he said. "The caustic solutions not only stop the super-iron from decomposing, but are basically the same as that used in alkaline batteries and therefore excellent for electrical energy storage."

Mr. Licht said he was exploring the commercial possibilities of super-iron batteries but added that it was too early to predict when they might go on the market and how much they would cost.

CHEMICAL & ENGINEERING NEWS
Volume 77, Number 33
CENEAR 77 (33) 1–72
ISSN 0009-2347
August 16, 1999

SUPERBATTERY HAS LONGER LIFE

New class of batteries employs unusual form of iron as cathode

A new class of light, environmentally benign alkaline batteries based on iron stores over 50% more energy than alkaline batteries that are currently available commercially.

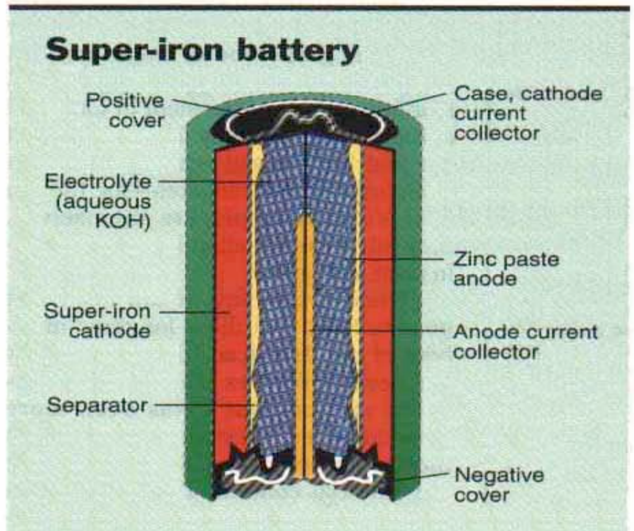
The "super-iron" batteries, as they are called, were developed by chemistry professor Stuart Licht, research associate Baohui Wang, and postdoctoral research fellow Susanta Ghosh at Technion-Israel Institute of Technology, Haifa [*Science,* **285,** 1039 (1999)].

The nonrechargeable alkaline batteries used in consumer electronic products contain a zinc anode, a manganese dioxide cathode, and a potassium hydroxide electrolyte.

The new battery replaces the heaviest portion of these batteries—the manganese dioxide—with "a very unusual material, super-iron, a material of which most scientists are unaware," Licht explains.

The batteries developed by Licht's group employ iron(VI)-containing compounds such as K_2FeO_4 or $BaFeO_4$ as cathode materials. Valence states greater than three are unusual for iron.

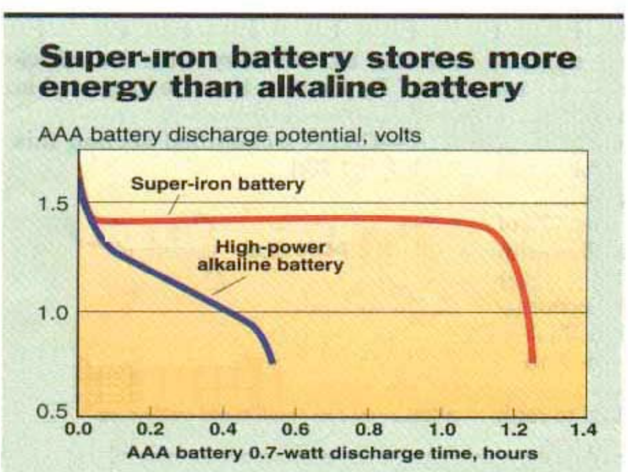
"In the past, the term 'ferrate' has been variously applied to Fe(II), Fe(III), and Fe(VI)," notes Licht, whose group prefers the term super-iron battery for cells containing Fe(VI). "Each iron atom is missing six electrons, so the material is capable of storing unusually high quantities of electricity."



During the cell discharge, Fe(VI) gains three electrons and is therefore reduced to Fe(III):

$$MFe(VI)O_4 + \tfrac{3}{2}Zn \rightarrow$$
$$\tfrac{1}{2}Fe(III)_2O_3 + \tfrac{1}{2}ZnO + MZnO_2$$
$$[M = K_2 \text{ or } Ba]$$

The discharge product, which includes the iron oxide Fe_2O_3, is relatively environmentally benign when discarded.



"The utilization of iron compounds as electrode materials is expected to reduce the price of a battery as well as to improve compatibility of batteries with our environment," comments battery expert Noboru Oyama, chemistry professor at Tokyo University of Agriculture & Technology. The compounds presented in this paper "are of great interest as a practical alternative to MnO_2."

Jeffrey R. Dahn, physics and chemistry professor at Dalhousie University, Halifax, Nova Scotia, characterizes the work of Licht and his team as excellent. "If this discovery can be commercialized, it will lead to a reduction in size and weight of portable electronics powered by nonrechargeable batteries," says Dahn, whose research interests include new materials for batteries.

He points out, however, that Fe(VI) compounds may have stability problems that could ultimately prevent commercialization.

But according to the Haifa researchers, Fe(VI) species are inherently stable. "Although the Fe(VI) species has been known for more than a century, its chemistry remains relatively unexplored, evidently due to a misperception that the Fe(VI) species is intrinsically highly unstable," they note.

After observing excess K_2FeO_4 in a concentrated potassium hydroxide solution over a few months, the researchers conclude that the compound can remain stable for many years, as long as it is free of nickel(II) and cobalt(II) impurities, which catalyze its decomposition.

Licht points to other benefits of the new battery. "Super-iron is highly conductive, which means that the super-iron battery may also discharge at rates more compatible with today's high-drain-rate electronics," he observes. "For example, a conventional AAA-size alkaline battery may last only a few minutes at a high drain rate, but under the same conditions, a AAA super-iron battery discharges for well over an hour."

The Haifa team has also shown that the super-iron cathode is compatible with secondary metal hydride batteries. "A cell with an iron(VI) cathode and a metal hydride anode is significantly (75%) rechargeable," the authors note.

The researchers are focusing further efforts on the single-use batteries, however. Engineering studies of the Fe(VI) cathode are ongoing, and research probing, stabilizing, and releasing the substantial storage of other Fe(VI) cathodes will be needed, they write. Such cathodes include a composite high-capacity Fe(VI) cathode containing several Fe(VI) salts.

Michael Freemantle

THE WALL STREET JOURNAL.

AUGUST 13, 1999 B8

Israelis' Rechargeable Battery May Last 50% Longer; Uses Unusual Form of Iron

By Robert Langreth
Staff Reporter of The Wall Street Journal

Researchers in Israel have developed a rechargeable battery that may last at least 50% longer than conventional batteries and someday could prove useful in a variety of consumer-electronics products.

The battery, invented by scientists at the Israel Institute of Technology in Haifa, is similar in design to existing alkaline batteries. But it takes advantage of a high-energy form of iron that is able to store more electrons than the energy-storing materials in existing batteries.

As a result, the scientists claim, the new battery can store 50% more energy than comparable-size conventional batteries. A description of the battery is being published in this week's edition of the journal Science.

Stuart Licht, a chemistry professor who led the Israel team, said the new battery design may be particularly useful for such devices such as cameras and cellular phones, which require a rapid discharge of electricity. That is because the new iron-based batteries may be able to last several times longer than conventional batteries, Dr. Licht said in an interview.

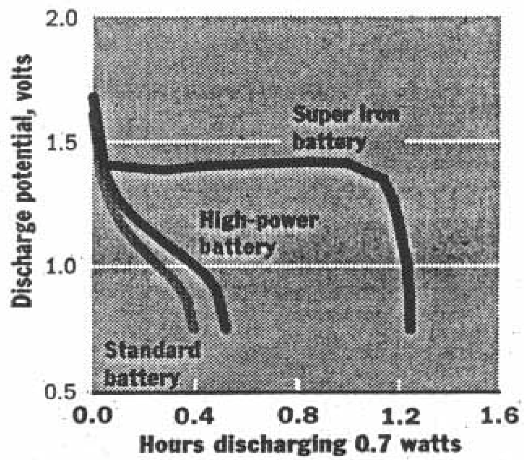
While promising, the batteries still are being tested in the laboratory. Dr. Licht said the technology is "patent protected," but he wouldn't comment on plans to commercialize it.

Batteries convert stored energy into electricity through chemical reactions that occur as electrons flow between a negatively charged anode and a positively charged cathode, which are electrodes inside a battery. In traditional batteries, the anode is typically made of zinc and the cathode is made with manganese dioxide.

To make its so-called super-iron battery, Dr. Licht's team replaced the manganese dioxide with an unusual form of iron called "iron (VI)." This iron can store more energy because each molecule can absorb more electrons from the anode than can manganese dioxide, the researchers

Super Iron, Super Juiced

AAA batteries employing "super iron" may last 50% longer or moare than current alkaline models.



Source: Stuart Licht, Israel Institute of Technology

thought to be too unstable to use in batteries and prone to disintegrate. But the Israel scientists found the instability disappeared when certain impurities were removed. Dr. Licht said the super-iron battery could be cheaper to make than conventional batteries.

In Boston, Ann Davin, spokeswoman for Gillette Co.'s Duracell division, said "we have been in contact" with the scientists. However, she said there haven't been any negotiations with them. "We think it's a technology that shows some promise, but more investigation is required."

Among the concerns about any new battery technology, she said, are whether it will work with current and future battery-driven products and how long a shelf life it has after manufacturing.

John Daggett, director of marketing services for the nation's No. 3 battery maker, Rayovac Corp., said he wasn't aware of the new technology.

—William M. Bulkeley in Boston and Kevin Helliker in Chicago

Science News
MAGAZINE OF THE SOCIETY FOR SCIENCE & THE PUBLIC
September 4, 1993

Sulfur-Aluminum Supercharges a New Battery

by Lipkin, Richard

Alkaline batteries, so the TV ads claim, keep on "going, and going, and going." Now, an experimental battery may keep on going, going, going even longer than the alkalines.

The new battery uses sulfur and aluminum to store charge, more than doubling the discharge time of a typical D-cell flashlight battery, says Stuart Licht, a chemist at Clark University in Worcester, Mass. Compared to other consumer batteries, such as those used in cars or radios, the experimental sulfur-aluminum aqueous cell holds more energy per pound, discharges longer, weighs less, and uses fewer noxious chemicals, Licht told a meeting of the American Chemical Society in Chicago last week. Licht and Dharmasena Peramunage, now at EIC Laboratories in Norwood, Mass., also report on the new battery in the Aug. 20 SCIENCE.

"This battery stores 220 watt-hours per kilogram and discharges up to 17 hours," says Licht. "In comparison, a good quality alkaline battery -- a D-cell for a flashlight -- stores 95 watt-hours per kilogram and discharges for about 6.5 hours. So far, we've only accessed 25 percent of our battery's theoretical capacity, which is over 900 watt-hours per kilogram. But we're confident we can get much more" than 25 percent.

The new battery uses a solid sulfur cathode to supply positive charge and an aluminum anode for negative charge. But there's a trick involved: To get solid sulfur (an insulator at room temperature) to conduct electricity, Licht and Peramunage bathed it in an aqueous polysulfide solution saturated with sulfur. To help the aluminum anode, they used a strong alkaline solution. The result: large stored charges and strong current flow.

"Sulfur and aluminum are wonderful chemicals for batteries," Licht says. "Aluminum is the most abundant metal in the Earth's crust, and we have piles of sulfur extracted from fossil fuels. They're both plentiful, cheap, lightweight, environmentally safe, and easy to work with."

Other types of batteries--such as lead-acid, nickel-cadmium, lithium, and sodium-sulfur systems--all have drawbacks, Licht contends. "Lead-acid and nickel-cadmium pose environmental problems, and they're heavy, so a car can't go far between recharges. Both sodium and lithium batteries explode if water touches them. And sodium-sulfur batteries operate above 600 [degrees] F, with safety and cost constraints." In contrast, he adds, the sulfur-aluminum cell runs at room temperature, storing seven times as much charge per pound as a lead-acid battery.

To be useful for electric vehicles, says Licht, a battery must win on two fronts: energy and power. The energy storage capacity measures how much charge it holds--the automotive equivalent of the size of the gas tank. Power measures how well the battery delivers "juice" to the engine for quick starts and fast acceleration. Licht says that, in theory, his battery does well in both areas, "with enough energy per pound to move a car several hundred miles before recharging--much farther than the 80 miles now possible with other batteries."

This galvanic tale is still unfolding. "We're only in the beginning stages, building tiny experimental cells," Licht says. "There's a long way to go before our battery reaches the marketplace."

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A Solid Sulfur Cathode for Aqueous Batteries

Dharmasena Peramunage and Stuart Licht*

Because of its high resistivity and subsequent low electroactivity, sulfur is not normally considered a room-temperature battery cathode. An elemental sulfur cathode has been made with a measured capacity of over 900 ampere·hours per kilogram, more than 90 percent of the theoretical storage capacity of solid sulfur at room temperature, accessed by means of a lightweight, highly conductive, aqueous polysulfide interface through the electrocatalyzed reaction $S + H_2O + 2e^- \rightarrow HS^- + OH^-$. This solid sulfur cathode was first used in a battery with an aluminum anode for an overall discharge reaction $2Al + 3S + 3OH^- + 3H_2O \rightarrow 2Al(OH)_3 + 3HS^-$, giving a cell potential of 1.3 volts. The theoretical specific energy of the aluminum-sulfur battery (based on potassium salts) is 910 watt·hours per kilogram with an experimental specific energy of up to 220 watt·hours per kilogram.

There is a critical need for new electrochemical storage concepts that address future societal needs for consumer batteries and the propulsion of electric vehicles (*1*, *2*). The search for contemporary batteries has blurred the conventional distinctions of electrochemical storage systems. For example, candidates for electrochemical propulsion include mechanically rechargeable primary batteries, secondary batteries, and fuel cells (*2*). There has been considerable interest in nonaqueous electrolytes (such as chloroaluminate), ambient-temperature molten

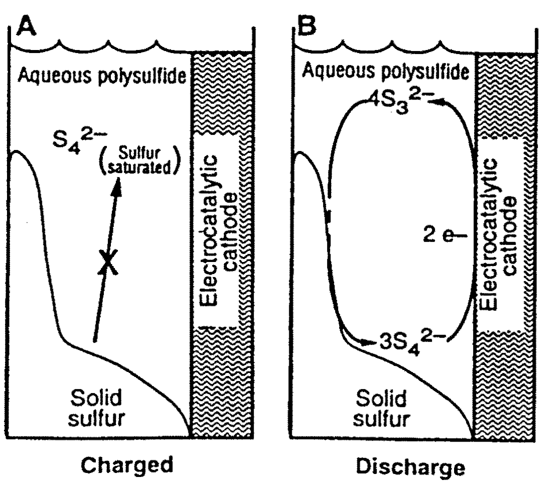

Fig. 1. Schematic representation of the solid sulfur cathode in its (**A**) charged state and (**B**) discharging state.

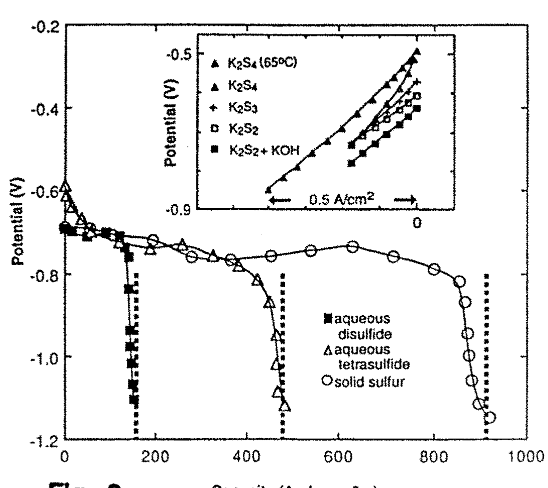

Fig. 2.

*To whom correspondence should be addressed.

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MARKETPLACE

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TECHNOLOGY & HEALTH

Battery May Make Electric Vehicles Much More Viable

By AMAL KUMAR NAJ
Staff Reporter of THE WALL STREET JOURNAL

Chemists at Clark University in Worcester, Mass., said they have developed a battery that may represent a significant step toward a viable electric car.

In the latest issue of Science, the researchers claimed that the battery provides six times as much power per unit of weight as the current lead-acid batteries being used in experimental electric vehicles. Moreover, they said the battery uses widely available and relatively low-cost materials, and runs at room temperature.

The battery's uniqueness lies in its coupling of sulfur and aluminum to generate electrical current, said Stuart Licht, a chemist who developed the battery with another chemist, Dharmasena Peramunage. Other types of batteries under development for electric cars include sodium-sulfur, nickel-metal hydride, nickel-cadmium and nickel-iron.

Mr. Licht said that most other batteries have significant disadvantages. The traditional lead-acid battery, he said, is too heavy and an environmental problem because of the lead content. The sodium-sulfur battery, which has been in development for nearly 20 years, is "promising on paper," he said, but it operates at temperatures between 600 and 700 degrees Fahrenheit that require expensive insulating. Also, sodium, like lithium, is explosive when it comes in contact with moisture.

"The batteries out there are either environmentally hazardous or can't power a car for large distances without a recharge," he said. "What we have is something very novel." But at the same time, Mr. Licht cautioned that the team's sulfur-aluminum battery is still in early stages of development.

Sulfur acts as the cathode, or positive terminal in the battery. Researchers converted the lightweight material, an insulator at room temperature, into a conductor by simply immersing it in a polysulfide solution. In contrast, in the sodium-sulfur battery, sulfur must be melted at temperatures above 600 degrees Fahrenheit to make it a conductor, he said.

The aluminum is the anode, or negative terminal. It's lighter than other materials currently used in batteries and stores more energy than, say, sodium. Also, it isn't a problem environmentally, like cadmium and lead, said Mr. Licht.

The chemist said their battery has demonstrated an energy capacity of as much as 200 watt hours per kilogram. The lead-acid batteries, on the other hand, provide 35 watt hours per kilogram, and enable cars to travel between 60 and 80 miles before recharge.