PreScouter

Disruptive Battery Technologies - 2018

Research Support Service

December 2018

Prepared by: **PreScouter**
Sofiane Boukhalfa, PhD I Project Architect
Navneeta Kaul, PhD I Researcher
Miriam Sousa, PhD I Researcher

PRESCOUTER

Question

What novel battery chemistries and technologies are currently under development that could potentially affect the current shape of the battery market over the next decade?

We are primarily interested in exploring novel chemistries that could potentially disrupt the market in the coming 5-10 years, and will exclude Li-ion battery chemistry developments (including solid state Li-ion, LiPo, etc…) from the search as these are well known and often profiled in the media.

Executive Summary

Results

- **10 disruptive battery technologies** were identified by the PreScouter team.
- Each technology is analyzed from both an academic research and commercial development perspective.
- Conclusions about the state of the technology and next steps are inferred from the collected data.

Insights

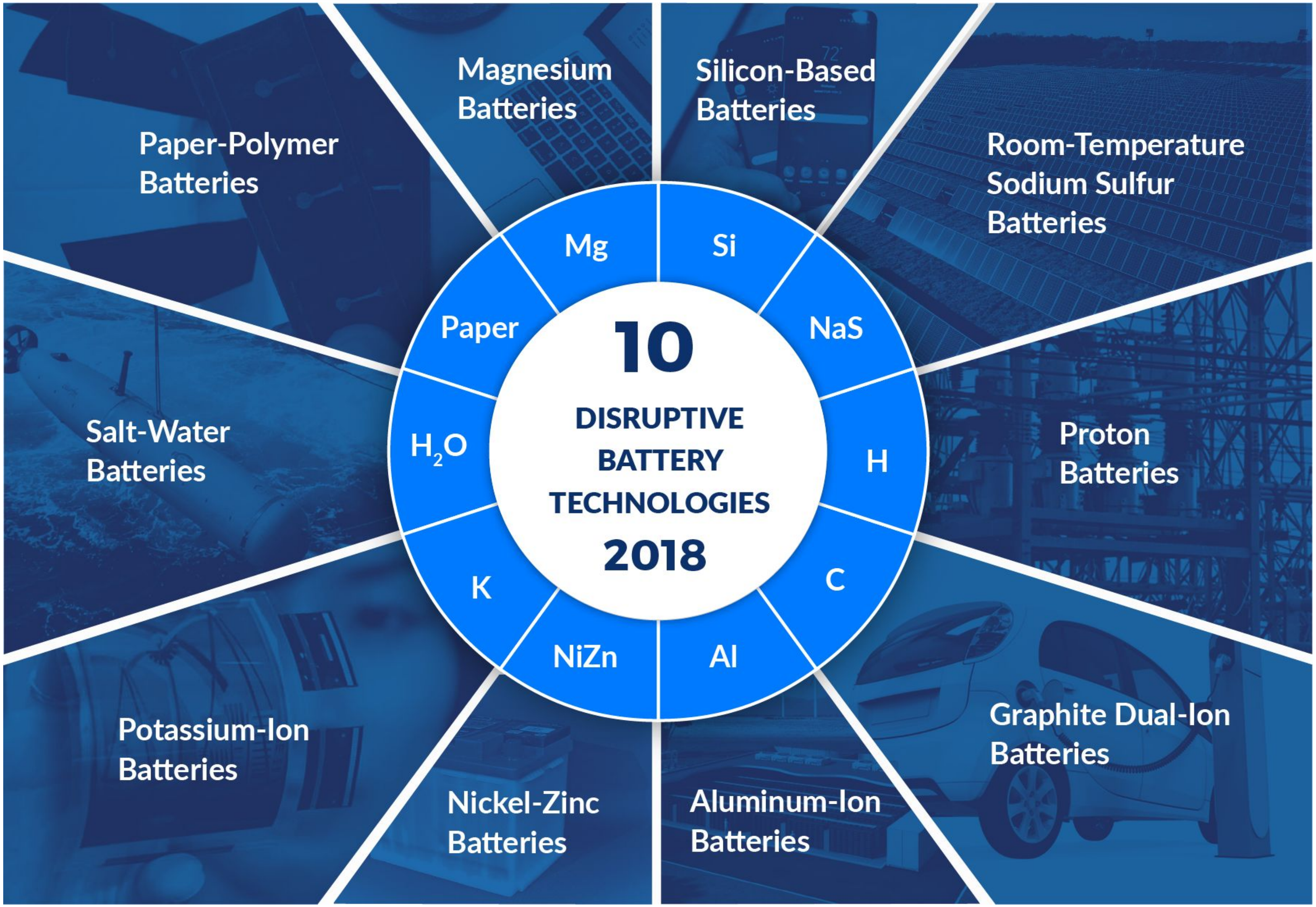
- Different chemistries optimized for different applications and market fit will likely determine the overall winner.
- Numerous chemistries are being developed to directly counter some of the disadvantages of Li-ion batteries, namely the high cost, and sourcing for the raw materials, as well as degradation of the battery caused by dendrite formation in the solid-electrolyte interphase (SEI).
- Nanotechnology is unlocking several approaches to improving performance of batteries.
- Most of these technologies are still in either the prototype or research phase, and may not appear on the commercial market until at least 5-10 years from now (with notable exceptions, e.g. silicon-based chemistries).
- Most of these technologies are aiming to reduce the cost of energy storage and point to new opportunities in the energy sector.

Executive Summary

Recommendations

- Most promising approaches offer alternatives to expensive Li material and theoretically offer higher energy and power density characteristics. Such chemistries are based on Silicon, Sulfur, Aluminum, and Magnesium. Of these, Silicon and Sulfur are closest to commercialization and may be the most worthwhile to investigate further.
- Note that Solid State and Lithium Polymer improvements will also have significant effects on the market over this period, but these were excluded from project focus in order to focus scope on more novel chemistries.

Technologies Presented in Report



10

DISRUPTIVE BATTERY TECHNOLOGIES

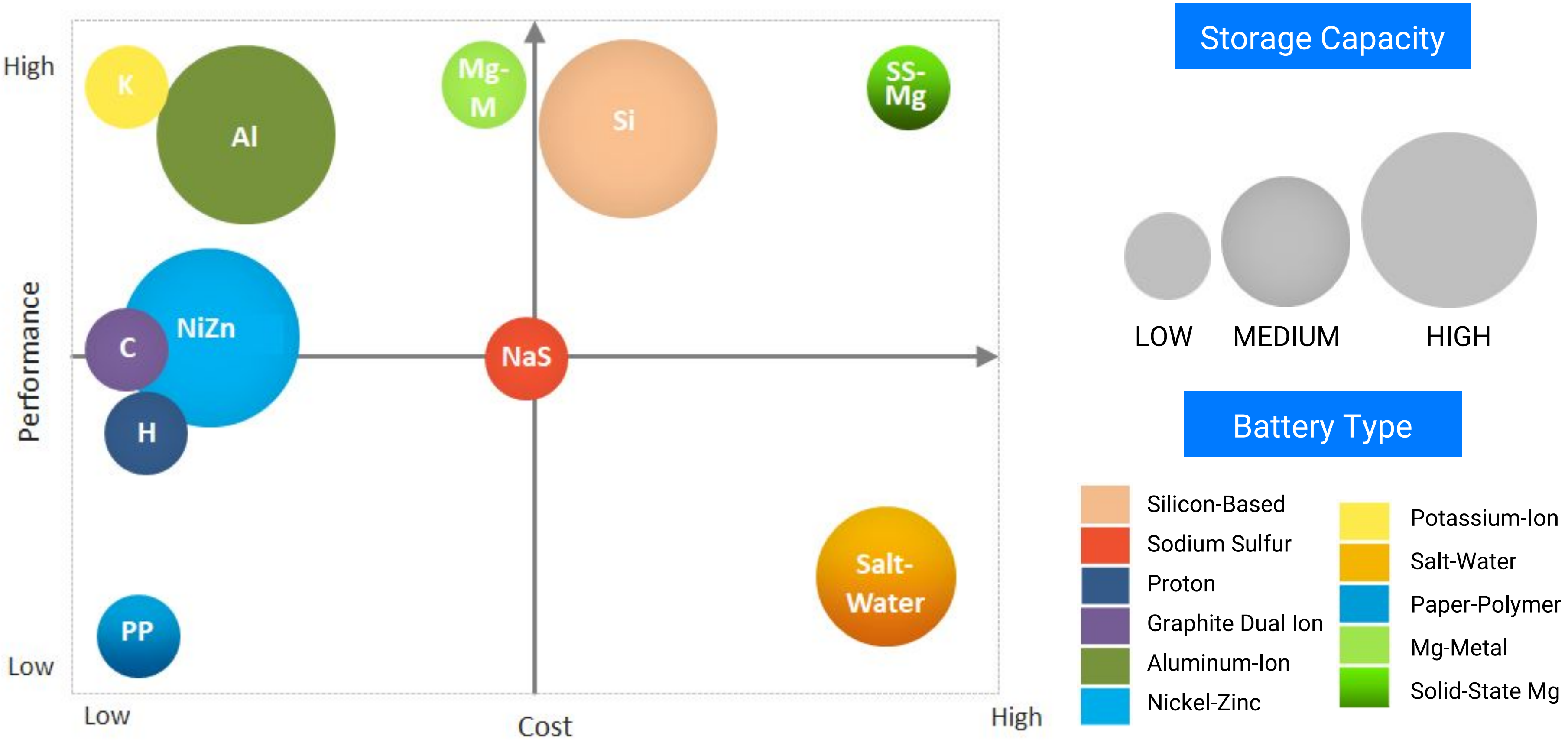
2018

Summary of Characteristics of Each Battery Technology

Battery Type	Phase	Cost	Performance	Capacity	Rechargeable	Applications	Page
Silicon-Based	Prototype	++	+++	+++	✓	Small electronics (e.g. smartphones, smartwatches), automotive	9
Room-Temperature Sodium Sulfur	Research	++	++	+	✓	Large-scale (like renewable energy grid storage), utility-scale load leveling	16
Proton	Research	+	++	+	✓	Automotive, infrastructure grid scale storage	23
Graphite Dual-Ion	Research	+	++	+	✓	Industrial, portable electronics, cars, grid-level applications	27
Aluminum-Ion	Research	+	+++	+++	✓	Grid-scale storage	33
Nickel-Zinc	Prototype	+	++	+++	✓	Automotive, renewables, electronics, telecom, marine	40
Potassium-Ion	Prototype	+	+++	+	✓	Flexible and bendable devices, grid-scale energy storage	46
Salt-Water	Prototype	++	+	++	✓	Utility-scale use, underwater autonomous vehicles, stationary energy storage systems	54
Paper-Polymer	Prototype	+	+	+	✗	Biosensors	60
Magnesium						Electronics, EVs, Grid-scale storage, etc.	64
Mg-Metal	Prototype	++	+++	+	✓		
Solid-State Mg	Research	+++	+++	+	✗		

+++ HIGH ++ MEDIUM + LOW

Cost vs Performance vs Storage Capacity



Battery Technologies

Silicon-Based Batteries

The modern world is running on Lithium-based batteries. Historically, engineers focused on making cathodes in these batteries from materials that can store ions more efficiently. Anodes, on the other hand, were still being made of graphite. A lot of companies are now focusing on making high-performance batteries using anodes made of silicon.

Silicon (Si) can bond with **25 times more** Lithium ions than graphite and therefore holds tremendous potential as an anode. Many start-up companies are involved in building the best Si dominant anodes for lithium-ion batteries.

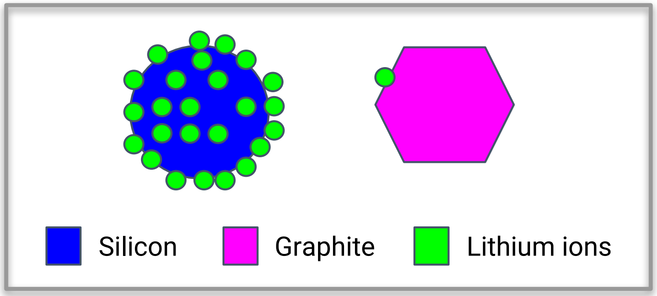


Figure: A schematic drawing comparing affinity of Si and graphite in bonding with lithium ions

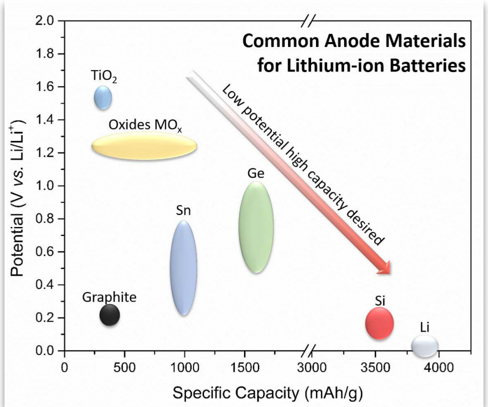


Figure: Graphical abstract from Current Progress of Si/Graphene Nanocomposites for Lithium-Ion Batteries

Advantages

- Relatively low voltage plateau
- Non-toxic
- Cost-effective
- Abundant in nature
- High theoretical capacity (3579 mA hg^{-1})

Limitations

- Low electrical conductivity
- Slow diffusion rate
- Undergoes huge volumetric fluctuations during lithiation

Silicon-Based Batteries

Research & Technology

The limitations presented on the previous slide result in Si pulverization and instability of the solid electrolyte interphase (SEI), leading to a loss of reversible capacity. To circumvent these changes, two primary approaches have been used: **nanotechnology & carbon coating**.

Nanostructured Silicon-Anode Materials: Nano-sized Si-based anodes involve reducing the particle size to nanosized particles. This improves the cycle life and rate stability compared to bulk-Si based anodes. Nanosized Si-based anodes have a **high surface area** which leads to low charge transfer resistance and can therefore, withstand lithiation and delithiation without cracking.

A higher rate of Li-ion transportation leads to an **enhanced rate performance** and **reduced pulverization**. Various nanostructured forms of Si have been used such as nanoparticles, nanowires and nanoporous structures with porous structures providing free space for Si volume expansion and a shorter path-length for lithium ion diffusion.

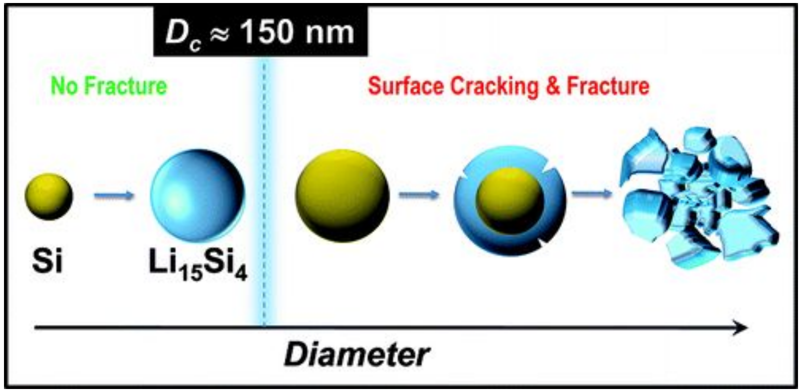


Figure: Size-dependent fracture of silicon nanoparticle.
Source: https://pubs.acs.org/doi/10.1021/nn204476h

Silicon-Based Batteries

Research & Technology

Si-based carbon composite Anode materials:

Carbon coatings reduce the volume expansion, increase the contact between Si particles and provide a stable SEI structure.

Nanosized Si in combination with different forms of carbon (C) materials have been investigated for high performance Si/C nanocomposite anodes. Recently, doped carbon with heteroatoms (N, B and S) have attracted considerable attention for coating agents, as they interact strongly with Li ions compared to carbon atoms.

Heteroatom-doped Si-C electrodes have better electrochemical properties with stable electrical conductivity. However, these reports are based off room temperature; the studies have not been performed at higher temperatures.

- In a recent study, published in Royal Society of Chemistry, N- and O-doped carbon coated (Si@CNO) composites prepared with micrometer-sized silicon and waterborne polyurethane (WPU) showed excellent electrochemical performance at 25^{0}C and 55^{0}C (see adjacent figure).

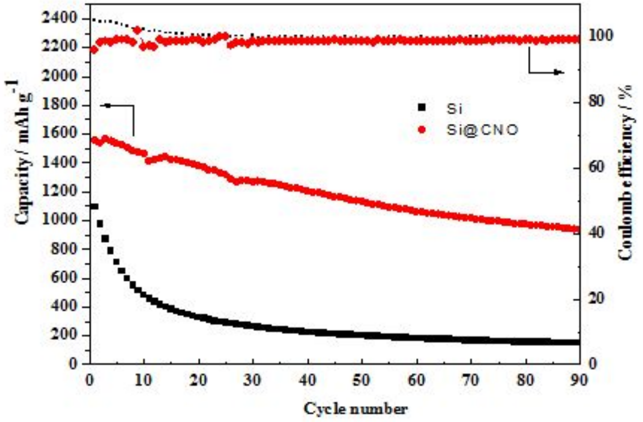


Figure: Capacity retention and coulomb efficiency curves of Si and Si@CNO versus cycle number at 55 °C.

Silicon-Based Batteries

Research & Technology

- Si/Graphene nanocomposite has demonstrated a lot of promise. Graphene, due to its excellent electrical conductivity, high surface area, superior chemical stability, and strong mechanical strength is being used in Si anodes.

- Crumpled capsules of graphene wrapped Si nanoparticles can overcome volumetric expansion of Si upon lithiation. Further, the 3D Si/graphene nanocomposite exhibits an excellent cycling stability and performance due to enhancement of the conductivity of the electrode by the 3D graphene network.

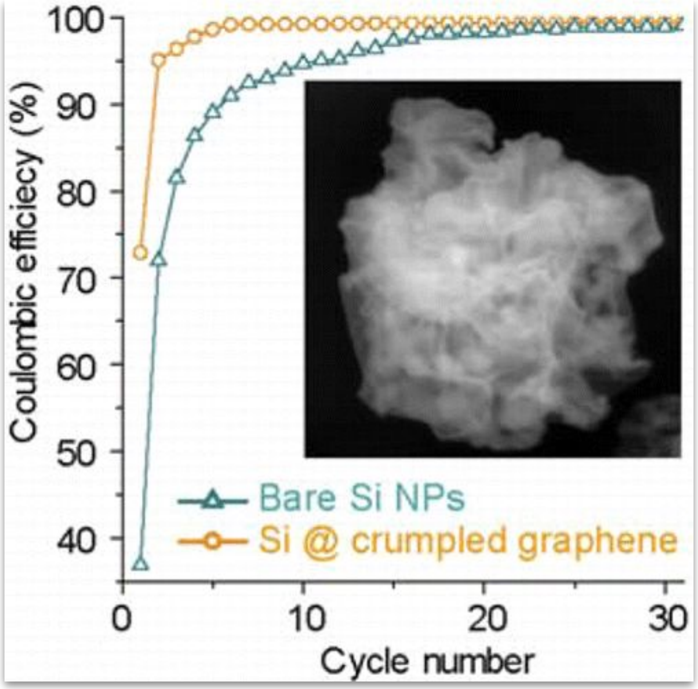


Figure: Graphical abstract from *Crumpled Graphene-Encapsulated Si Nanoparticles for Lithium Ion Battery Anodes*

Silicon-Based Batteries

Commercial Developments

CLOSE TO COMMERCIALIZATION

SILA NANOTECHNOLOGIES

Sila Nanotechnologies, a start-up based in California, has used the porous nature of nanoparticles to secure the battery from swelling and shattering. They have shown an enhanced battery performance of up to 40%. The method involves packing silicon atoms inside a matrix of empty nanoparticles. When the silicon anode binds lithium ions, these ions fill up the empty spaces and do not push silicon atoms apart.

The startup just won $70 million of venture funding to commercialize the technology and expects the batteries to work with the consumer electronics **starting early 2019**. The company intends to use the cash to build a facility in Silicon Valley to produce about 20-MWh worth of batteries annually. Roughly, this would be enough to power 2-10 million smartwatches.

Earlier this year, **BMW** partnered with the company to incorporate the SILA Nano batteries into vehicles by 2023 to increase energy capacity by 10 to 15%. They have also joined hands with **Amperex Technology**, one of the major suppliers of batteries to Apple and Samsung.

Figure: Prototype of Sila Nanotech battery.
Photo credits: Sila

Silicon-Based Batteries

Commercial Developments

The competition in the market is fierce with start-up companies like **Enovix**, **Angstron Materials**, and **Enevate** promising to build silicon dominant lithium-ion batteries.

OTHER COMPETITORS

- ➔ Enovix, backed by Intel and Qualcomm claims to make lithium-silicon batteries capable of packing 50% more energy into a smartphone.
- ➔ Similarly, silicon anodes produced by Angstron Materials and Enevate are being tested by car companies and electronics companies.

Silicon dominant lithium-ion batteries promise to lower costs and add capabilities to cars and smartphones.

Silicon-Based Batteries

Conclusion & Future Outlook

Intense research is going on to improve Si-anode materials. Nanotechnology and silicon-based composite anodes are being used to address the challenges of volumetric expansion. However, research needs to be carried out for improving high power density, prolong life, ease manufacturing and lower the cost.

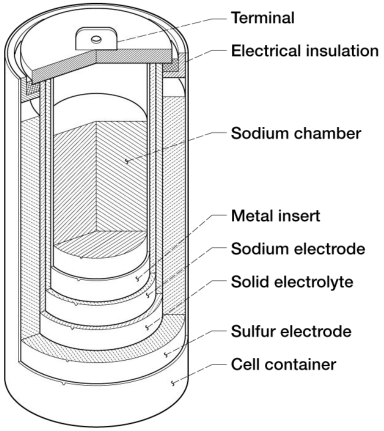
References

1. https://www.technologyreview.com/s/610792/this-battery-advance-could-make-electric-vehicles-far-cheaper/
2. https://qz.com/1360234/a-silicon-valley-startup-is-giving-lithium-ion-batteries-a-much-needed-silicon-boost/
3. https://www.wsj.com/articles/the-battery-boost-weve-been-waiting-for-is-only-a-few-years-out-1521374401
4. https://venturebeat.com/2018/08/16/sila-nanotechnologies-raises-70-million-for-next-generation-battery-development/
5. https://www.sigmaaldrich.com/technical-documents/articles/materials-science/recent-developments-in-silicon-anode-materials.html
6. http://rsos.royalsocietypublishing.org/content/5/8/180311
7. https://www.mdpi.com/2311-5629/4/1/18
8. https://pubs.acs.org/doi/10.1021/nn204476h
9. https://pubs.acs.org/doi/10.1021/jz3006892

Room Temperature Sodium Sulfur Batteries

Sodium-sulfur (NaS) batteries are one of the most promising alternatives for lithium-sulfur (LiS) batteries due to similar physical and chemical properties of Na and Li ions. However, the batteries fall into the category known as high-temperature batteries as high temperatures (> 300^0C) are required to maintain the Na anode and cathode at a molten state for battery operation.

Such high temperatures not only increase the cost of operation and maintenance, but also raises serious safety concerns by molten Na and S. Molten polysulfides produced after the reduction of S at the cathode are also corrosive at high temperatures which further restrains the widespread application of high temperature Na-S batteries. As a result, the low-cost room temperature (RT)/NaS battery system is arousing extensive research interest for use in large-scale applications with increased safety.



Cut-away schematic of Sodium-sulfur battery.

Advantages

- Similar physical and chemical properties of Na and Li ions
- Suitable for renewable grid scales

Limitations

- Low capacity
- Brittle and fragile nature of the beta alumina ceramic electrolyte membrane
- Not suitable for cars and phones

Room Temperature Sodium Sulfur Batteries

Research & Technology

A RT/NaS battery requires a Na anode, a sulfur-containing composite cathode, Na salts dissolved in an electrolyte and a thin membrane between them as separator that allows ion conduction. In practice, the capacity of RT/NaS batteries is much lower than the theoretical capacity due to complex reactions within the battery.

To solve these problems, multiple strategies have been reported in 2018 especially those focusing on the **membrane, modification of electrolytes, and design of electrodes**.

1) Replacing the ceramic membrane

One of the limiting factors in the development of RT-NaS batteries is the brittle and fragile nature of the beta alumina ceramic electrolyte membrane between the molten anode and cathode components. During operation, this paper-thin membrane gets easily damaged. A research group led by Dr. Sadoway at **MIT** reported a breakthrough approach to circumvent the issue. The team realized that the functions of the membrane could get performed by a specially coated metal mesh, a much stronger and more flexible material that could stand up to the rigors of industrial-scale storage systems.

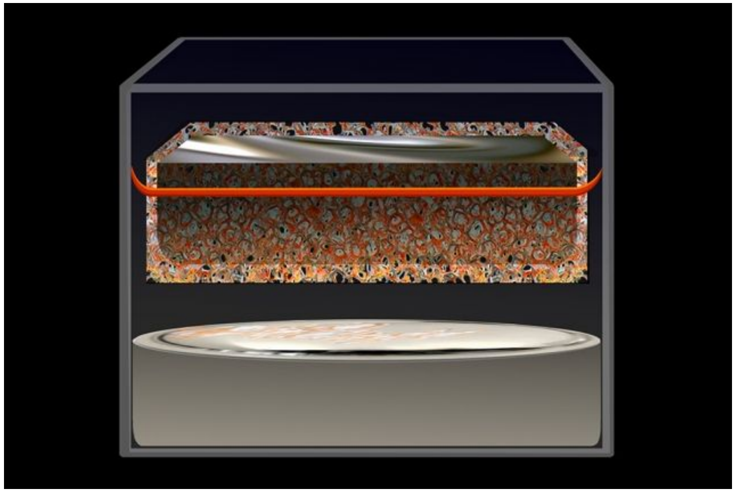


Figure: A new approach to rechargeable batteries. RT/NaS battery with a metal mesh membrane. Source: MIT.

Room Temperature Sodium Sulfur Batteries

Research & Technology

MIT's Technology: After a series of experiments, a steel mesh coated with a solution of titanium nitride yielded the best results. The membrane is electronically conductive and achieves chemical selectivity by faradic reaction instead of regulated ionic conduction, without the brittleness and fragility. It could be applied to a wide variety of molten-electrode battery chemistries and opens up new avenues for battery design. This approach offers the following benefits:

- A whole set of durable, inexpensive, safe NaS batteries could be made with abundant raw materials.
- Batteries could undergo many cycles of charge-discharge without degradation.

These advantages could make NaS batteries suitable for renewable grid scale installations capable of delivering steady baseload electricity. However, these batteries would not be usable for cars or phones.

2) Atomic cobalt as an efficient electrocatalyst in sulfur cathodes

Recently, sulfur cathodes with inherent polarization such as metal oxides and metal sulfides have been investigated for NaS cells. Compared to carbon materials, these polarized materials consist of a strong intrinsic sulfiphilic property, which leads to a strong chemical interaction between the polar host materials and polysulfides and obstructs polysulfide dissolution.

Room Temperature Sodium Sulfur Batteries

Research & Technology

A research group from the University of Wollongong, Australia in 2018 successfully synthesized a highly effective **sulfur cathode with atomic cobalt (Co)** supported in micropores of hollow carbon (HC) nanospheres. The HC nanospheres anchor Co nanoparticles and encapsulate sulfur. In each HC reactor, diffusion of sulfur molecules serves as the traction for atomic Co into carbon shells, forming a novel Co-HC host. In RT-NaS batteries, this synthesized cathode exhibits outstanding electrochemical performance as Co enhances sulfur reactivity and electrocatalytically reduces polysulfide into the final product, sodium sulfide.

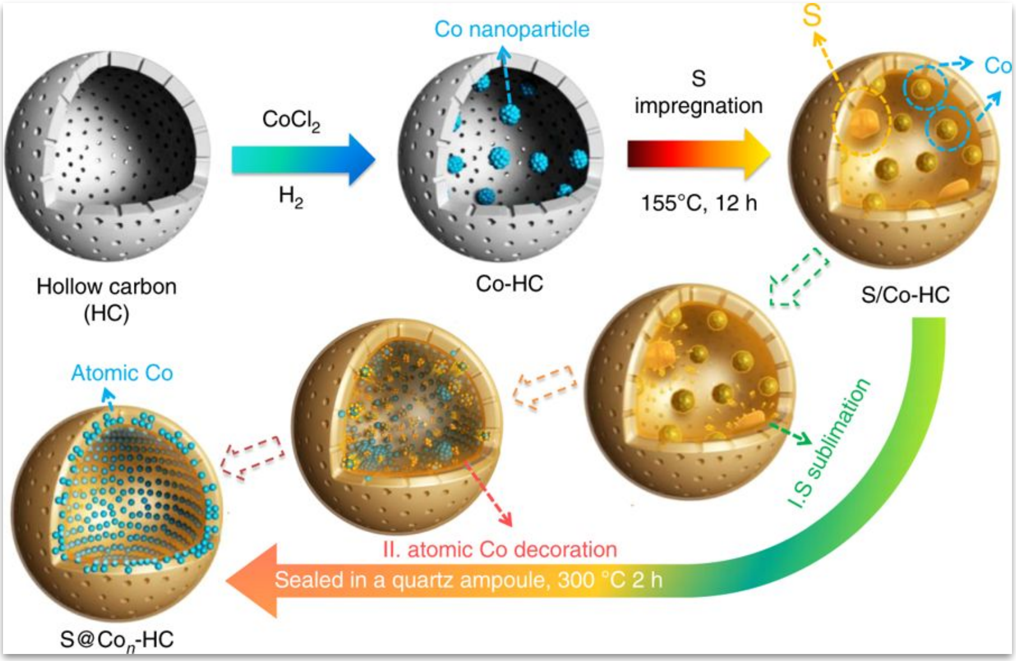


Figure: Schematic illustration of the synthesis of the hollow carbon decorated with cobalt nanoparticles (Co-HC). After sulfur (S) impregnation, the S/Co-HC is heat treated to generate atomic Co-decorated hollow carbon as a sulfur host material ($S@Co_n$-HC).

Room Temperature Sodium Sulfur Batteries

Research & Technology

More specifically, the S@Co-HC cathode offers a cycling stability (507 mA h g^{-1} after 600 cycles at 100 mA g^{-1}) and rate performance (220.3 mA h g^{-1} at 5 A g^{-1}). Additional mechanistic data from cyclic voltammetry (CV), Raman spectroscopy, synchroton X-ray diffraction (XRD), and density functional theory (DFT), confirms the electrocatalytic effects of atomic Co. **The present research introduces atomic Co in the electrode design, could steer the design of new electrode materials for RT-NaS batteries.**

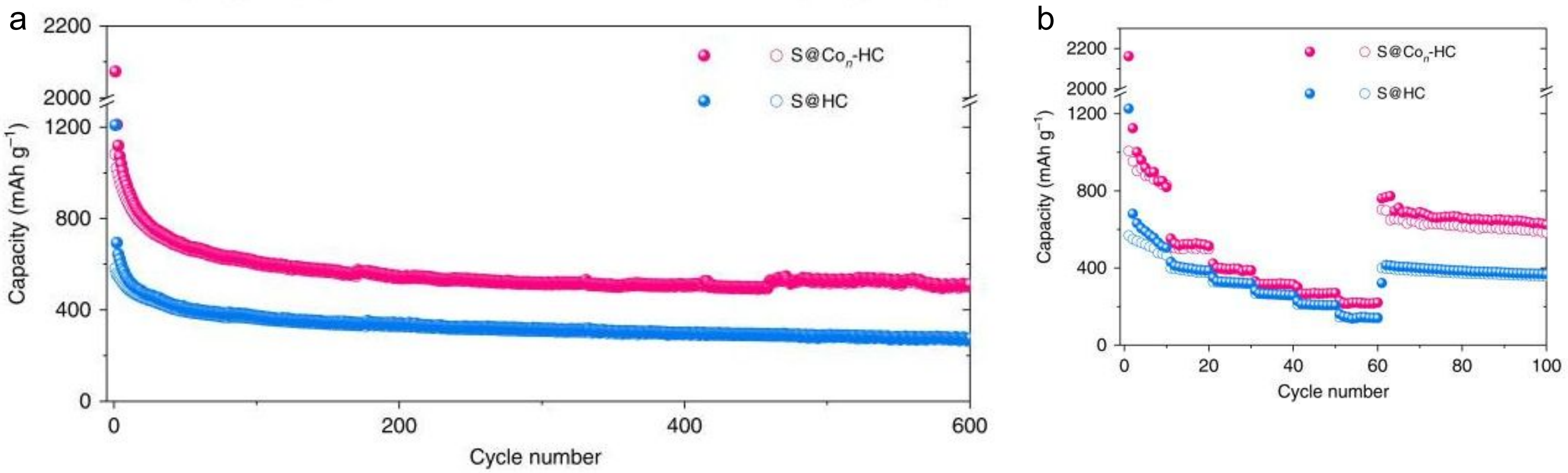


Figure: Room-temperature sodium-sulfur battery test. **a**, **b** Cycling performance and rate performance for S@Co*n*-HC and S@HC.

Room Temperature Sodium Sulfur Batteries

Research & Technology

3) Multifunctional electrolyte

Optimizing the components of the electrolytes have been proposed as one of the promising approaches to address the drawbacks of RT-NaS batteries without compromising the energy density or tedious production process. Recent research published in **Nature** reports a RT-NaS battery with **high electrochemical performances** and **increased safety** by employing a multifunctional-carbonate electrolyte. It contains propylene carbonate (PC) and fluoroethylene carbonate (FEC) as co-solvents, highly concentrated bis(trifluoromethane)sulfonimide sodium (NaTFSI) salt, and indium triiodide (InI_3) additive.

Through a series of experiments, the group demonstrates that the fluoroethylene carbonate solvent and high salt concentration results in the reduction of the solubility of sodium polysulfides, and a robust SEI on the Na anode upon cycling. **The electrolyte design strategy can be employed to a wide range of Na-based rechargeable battery systems, and advance the development of low-cost and high-performance energy storage devices.**

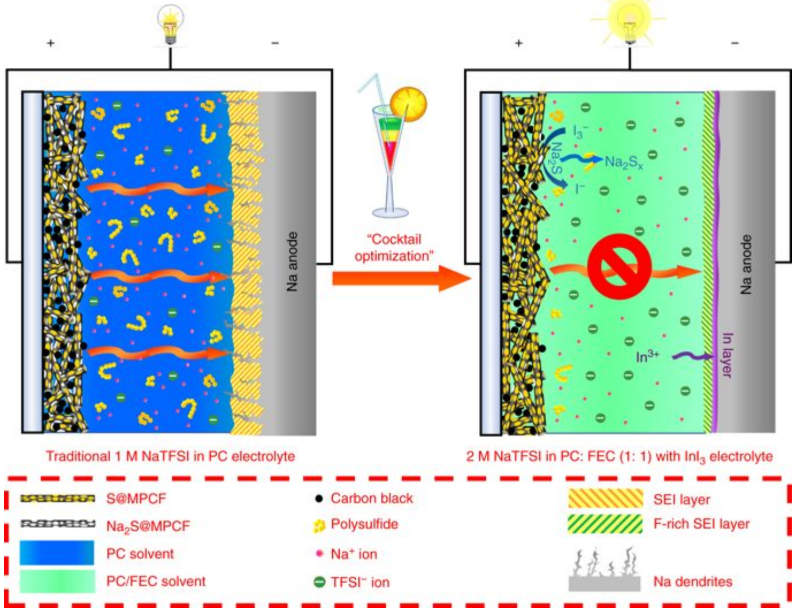


Figure: Schematic illustration of the electrolytes with conventional 1M NaTFSI in PC electrolyte and (right) 2MNaTFSI in PC:FEC with 10mM InI3 additive electrolyte

Room Temperature Sodium Sulfur Batteries

Commercial Developments

The Japanese company, **NGK** manufactures almost all NaS batteries for grid storage. NaS batteries are expected to improve in performance, installation and operating costs. However, more companies are required to spur the innovation in the market. **Ambri**, a spin-out company from MIT, led by Dr. Sadoway, founder and lead researcher involved in the breakthrough technology of replacing the ceramic membrane with steel mesh, is working to improve RT-NaS batteries.

NOTABLE COMPANIES

Conclusion & Future Outlook

Currently, only high-temperature NaS batteries have been commercialized for grid storage, while RT-NaS batteries are still in the early phase of development. However, with recent advancements in electrolyte design, sulfur cathodes, and battery design, the performance of NaS batteries has significantly improved. On-going research is expected to pave the way for the development of next-generation NaS-based energy storage technologies.

References

1. https://www.designnews.com/content/return-sodium-sulfur/150501763958615
2. https://www.nature.com/articles/s41560-017-0072-1
3. https://news.mit.edu/2018/metal-mesh-membrane-rechargeable-batteries-renewable-energy-0122
4. https://www.sciencedirect.com/science/article/pii/S2468025718300013
5. https://www.nature.com/articles/s41467-018-06144-x
6. https://www.nature.com/articles/s41467-018-06443-3

Proton Batteries

The proton battery concept was first proposed in 2014 by Professor Andrews, from RMIT. The team built a prototype based on a metal-hydride-Nafion composite electrode for storing hydrogen (*see Figure below*). However, the battery suffered from a variety of issues including low reversibility, less electrochemical hydrogen storage and expensive metal alloys used for manufacturing electrodes.

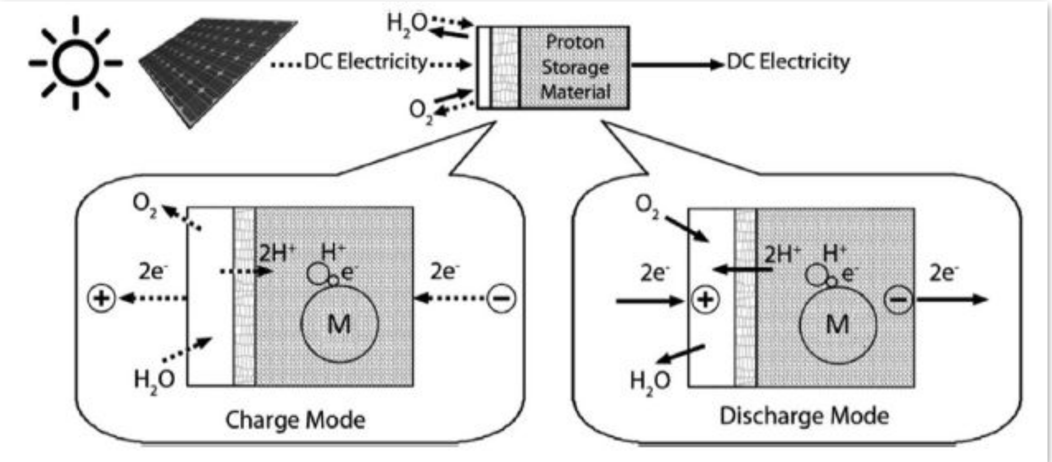


Figure: The novel battery concept as proposed in 2014 by Professor Andrews from RMIT. During charging, the electricity applied to a catalyst splits water into protons and oxygen. The protons travel through a Nafion membrane and get stored in the solid-state electrode. While discharging, the protons, pass back through the membrane and combines with the oxygen to produce electricity and water vapor, like a standard fuel cell.

Advantages

- Environmentally-friendly with zero emissions (carbon doesn't burn)
- Comparable efficiency to a Li-ion battery
- More lightweight and a compact than Li-ion batteries

- Low storage capacity
- Low reversibility
- Low current density
- Multiple charge and discharge cycles tests need to be done

Limitations

Proton Batteries

Research & Technology

A traditional Proton exchange membrane (PEM) fuel cell uses platinum catalysts to combine hydrogen and oxygen from the atmosphere to produce electricity, water vapor, and heat. However, the production, transportation, and storage of hydrogen gas are challenging thus hindering the widespread use of PEM cells.

The viability of PEM fuel cells in the transportation sector remains a challenge due to the cost of production, transportation, and storage of hydrogen gas.

A team of researchers at **RMIT University** in Melbourne, Australia have reported the technical feasibility of a proton battery for the first time. The battery is composed of two parts, a carbon electrode that stores hydrogen or protons from water and a reversible PEM fuel cell that generates electricity from the hydrogen.

In the newest version, the **electrode** used is an **activated carbon** fabricated from phenolic resin which replaces the metal alloys from the 2014 version as the hydrogen electrode. Carbon is cheap, abundant, structurally stable with a large internal area for hydrogen storage, and has a much lower atomic mass than the previously used metal alloys, leading to a cheaper, lighter and high-performance battery. Another significant design innovation is the use of a small volume of **liquid acid** inside the **porous material** to conduct protons as hydronium to and from the Nafion membrane of the reversible cell.

Proton Batteries

Research & Technology

The research was published in the International Journal of Hydrogen Energy in 2018, and the results demonstrated the ability of the carbon electrode to store nearly 1% (by weight) of hydrogen in charge mode and release 0.8% (by weight) in discharge (electricity supply) mode. A voltage of 1.8 V was reached with the battery.

CARBON ELECTRODE

Stored	Released
1%	**0.8%**

(by weight) of hydrogen in charge mode and discharge mode, respectively

A VOLTAGE OF

1.8 V

reached with the battery

Commercial Developments

The commercialization of the proton battery is still a long way off. The RMIT team estimates that the proton battery will be commercially available within 5-10 years. ABB Marine and Sintef Ocean announced in November a new research project to test a megawatt-scale propulsion plant using two 30 kW hydrogen fuel cells. The project seeks “to provide answers for fuel cell technology delivered at the scale needed to power commercial and passenger chips,” as stated in the joint press release.

Proton Batteries

Conclusion & Future Outlook

This is a major advancement for efficient hydrogen-powered energy production. The most dominant material used in batteries, lithium, is expensive and scarce. The proton batteries do not use Li at all, and aside from using small amounts of platinum as a catalyst, the remaining materials are inexpensive and abundant. With an increase in the volumetric density of the proton battery, it could be a contender to the current Li-ion batteries.

Although, the technology is groundbreaking, the battery system is still far from being optimized. The team aims to increase the voltage to 2V in future designs. Future work will be focused on the use of graphene in proton batteries to make them even more efficient. Another area of focus for the researchers is to understand the nature of interactions between the hydrogen ions and the surface of the pores within the carbon electrode. The promise of meeting higher energy demand with lower cost, readily available carbon is nevertheless a breakthrough.

References

1. https://www.greenoptimistic.com/worlds-first-rechargeable-proton-battery-invented-at-rmit-in-australia-20180524/#.W9jcZ3pKj-Y
2. https://www.designnews.com/electronics-test/proton-battery-could-offer-lithium-ion-alternative/185362264658390
3. https://www.theguardian.com/technology/2018/mar/09/look-no-lithium-first-rechargeable-proton-battery-created
4. https://www.sciencedirect.com/science/article/pii/S0360319918302714
5. https://www.sciencedirect.com/science/article/pii/S0360319913027341
6. https://www.marinelink.com/news/abb-sintef-test-hydrogen-fuel-cells-443458

Graphite Dual Ion Batteries (DIBs)

As another potential alternative to Li-ion batteries for large-scale stationary storage of electricity, dual-ion batteries (DIBs) have attracted significant attention in recent years. DIBs use abundant metals including K, Mg, Ca and Al as electroactive ionic species instead of Li. However, they lag behind Li-ion batteries due to lower energy density and the need for large quantities of electrolyte solutions, as the ion-solutions are required for the electrode charge and discharge respectively. So far, with the moderately concentrated electrolyte solutions of 0.3-0.1M, DIBs have resulted in a lower energy density of 20–70 Wh kg^{-1}. Research efforts are on to increase the energy density by maximizing the ionic content of the electrolyte without compromising on the ability of the electrodes to store charge and the voltage of the battery.

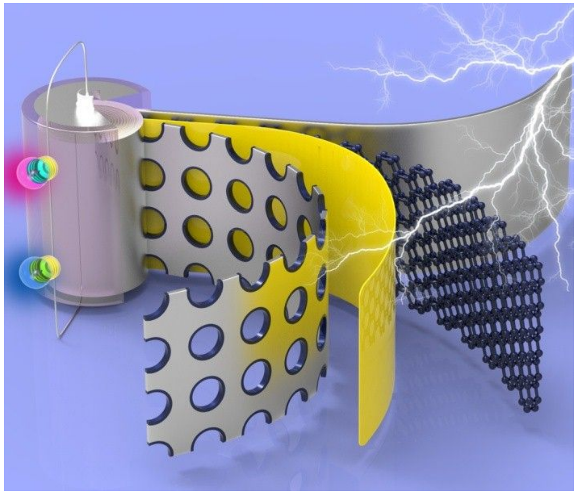


Figure: Schematic structure of the DIB designed by the Chinese Academy of Sciences in 2016. Image credit: TANG Yongbing

Advantages

- Low cost
- Long-term cycling capabilities
- High rate performance

Limitations

- Lower energy density than Li-ion batteries
- Requires large quantity of electrolyte solutions
- Large volumetric changes in the electrodes during the intercalation

Graphite Dual Ion Batteries (DIBs)

Research & Technology

1) KFSI-graphite DIB with highly concentrated electrolyte

In research published in Nature communications on 26th October 2018, scientists have demonstrated a new lithium-free graphite dual-ion battery using a graphite cathode and potassium anode, known as graphite dual-ion battery (GDIB).

The team focused on identifying **Li-free electrode-electrolyte combinations** for DIB to increase the energy density of the cell. The researchers determined the melting temperatures and ionic dimensions of monovalent anions that could intercalate into graphite and could also be available as Li-free salts. They chose **ethylene carbonate/dimethyl carbonate (EC/DMC)** as a solvent due to its highest **electrochemical stability** window of up to 6V. The team used a highly concentrated solution of 5 M potassium bis(fluorosulfonyl)imide, KFSI, in alkylcarbonates and selected **FSI salts** due to its **low melting point** and relatively **small ionic size**.

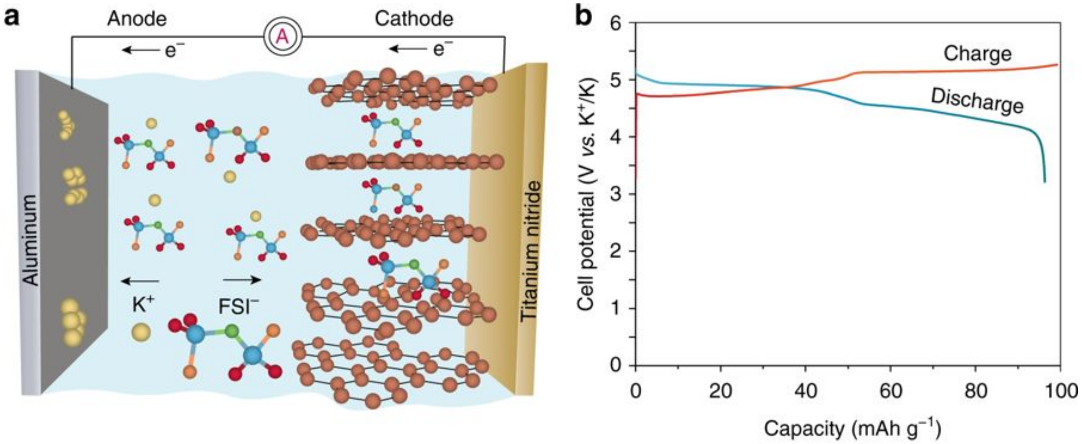


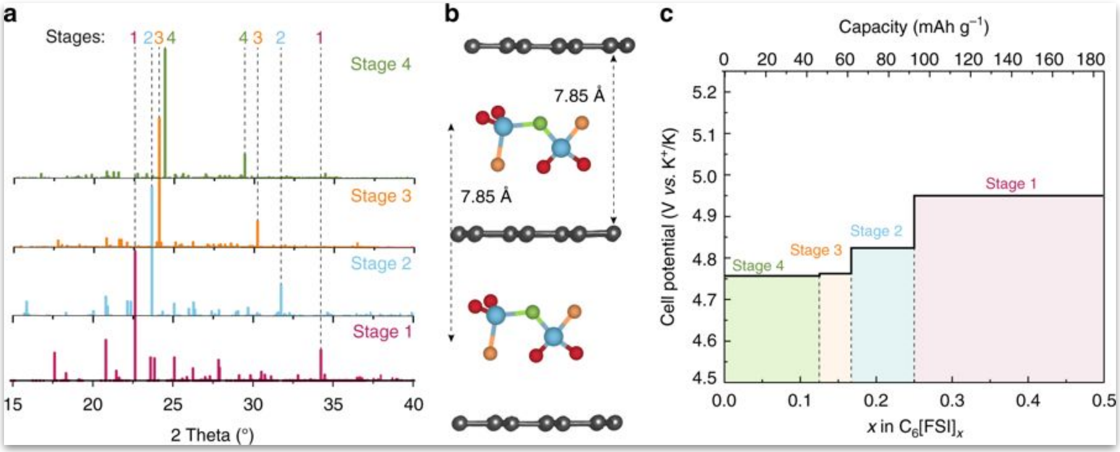
Figure: Working principle and energy density of KFSI-graphite DIB. **(a)** Schematic of the charging process in KFSI-graphite DIB. Fluorine, oxygen, sulfur, and nitrogen atoms in the FSI^- anion are shown in brown, red, blue, and green colors, respectively. **(b)** Typical galvanostatic voltage profile of KFSI-graphite DIB measured at a current density of 50 mA g^{-1}.

Graphite Dual Ion Batteries (DIBs)

Research & Technology

GDIB works as a dual-ion battery by utilizing the reversible intercalation of anions into the graphite cathode during charging. Metal electroplating intercalation or alloying reactions take place on the anode side. FSI anions intercalate into graphite during charging, as confirmed with solid-state F NMR spectra, X-ray diffraction (XRD) and computationally while K electroplates on the Al current collector. The KFSI-graphite DIBs demonstrate energy efficiency at par with Li-ion batteries. The battery exhibits an energy density of 207 Wh kg−1, along with a high energy efficiency of 89% and an average discharge voltage of 4.7 V.

Figure: DFT calculations of FSI$^-$ anion intercalation into graphite. a Simulated powder XRD patterns of charged graphite with intercalated FSI$^-$ anions in different stages. b Schematic of FSI$^-$ anion intercalated into graphite for stage 1 (*n* = 1).c Calculated voltage profile of FSI$^-$ anion intercalation into graphite as a function of the molar ratio between FSI$^-$ and C (i.e., *x* in C6[FSI]*x*)



GDIB appears to be a strong competitor among existing electrochemical cell concepts for grid-level batteries. Currently, the team is working to optimize the battery design to support large volumetric changes in the electrolyte and electrode during the intercalation process.

Graphite Dual Ion Batteries (DIBs)

Research & Technology

2) First graphite-graphite dual ion battery based on Al salt electrolytes

Dual ion-batteries based on Al salts have not developed until now. A recently published research detailed a novel graphite-graphite dual ion battery (GGDIB) based on AlCl3/1-ethyl-3-methylimidazole Cl ([EMIm]Cl) room temperature ionic liquid electrolyte.

The GGDIB demonstrates great cycle and rate performance due to the high ionic conductivity of the ionic liquids. The battery is environment-friendly, inexpensive and the design is useful for future energy storage applications.

The team used X-ray photoelectron spectroscopy (XPS) to study the mechanism of electrochemical reaction mechanism and high-resolution transmission electron microscopy for the analysis of the charge/discharge mechanism of the graphite cathode and anode of the battery. The results demonstrate that $AlCl_4$ is reversibly intercalated and deintercalated in the graphite cathode. Al gets reversibly deposited and dissolved on the surface of the graphite anode during charging and discharging while chloroaluminate ions get intercalated in the cathode material. However, the electrochemical polarization increases gradually with the increasing current density leading to the attenuation of its capacity.

In the future, the team is interested in studying the **self-discharge phenomenon**. They intend to form a dense SEI film on the surface of the electrode material by adding additives to the electrolyte for the study. Further experiments will lead to further improvement of the battery.

Graphite Dual Ion Batteries (DIBs)

Research & Technology

3) Zn/graphite dual ion battery

Zn-dual-ion battery based on the anion (trifluoromethanesulfonate, TfO^-) intercalation into the graphite cathode was rarely reported. Recent research has presented a zinc/graphite dual ion battery with graphite as the cathode, Zn as the anode. It works on the basis of the electrolyte Zn2+ deposition on the zinc anode and TfO^- intercalation into the natural graphite cathode. During discharging, both ions are released back into the electrolyte.

To investigate the feasibility of the battery system, deposition of zinc on a copper or zinc substrate and the reversible intercalation of the of TfO^- into graphite were studied by cyclic voltammetry (CV), XRD, and SEM tests. The SEM images show that zinc deposits are compact, dense and distribute uniformly on anodes **without the formation of dendrites**.

Therefore, the ionic liquid electrolyte suppresses the formation of dendrites on the Zn surface. Zn^{2+} cations are mobile in the ionic liquid electrolyte and therefore can be deposited and stripped in this electrolyte. The electrolyte has several attractive features including low volatility, non-flammability, and high thermal stability, leading to safe batteries. The experiments reveal that the insertion of TfO^- into/from graphite is a reversible process. Currently, the team is focusing on improving the graphite intercalation capacity with the system to improve the overall performance of the Zn/graphite dual-ion cells.

Graphite Dual Ion Batteries (DIBs)

Commercial Developments

The technology is still in its infancy and needs further testing and optimization before entering the next phase of commercialization.

Conclusion & Future Outlook

Overall, intensive research efforts are on to improve the battery design of non-Li graphite based dual-ion batteries before commercialization. With multiple advantages including low cost, high rate performance, high energy-density, and long-term cycling capabilities of GDIBs have tremendous potential to be used for industrial applications, high energy field, EVs and portable electronics.

References

1. http://english.cas.cn/newsroom/research_news/201610/t20161008_168391.shtml
2. https://www.nature.com/articles/s41467-018-06923-6
3. https://link.springer.com/article/10.1007/s11581-018-2644-x
4. https://www.ncbi.nlm.nih.gov/pubmed/29882341

Aluminum-Ion Batteries

Aluminum is being investigated as a potential replacement for Li in batteries and offers numerous advantages. Aluminum is readily available, inexpensive and more abundant than lithium. Al when used as an anode in a battery, can release three electrons during discharging, compared to a single electron released by Li. Moreover, Al does not result in dendritic formation during charging.

In an aluminum ion battery, Al forms a complex with chlorine from the electrolyte to make two mobile ionic charge carriers, $AlCl_4^-$ and $Al_2Cl_7^-$. These chloroaluminate anions pass from the Al metal anode, through the electrolyte to the graphite cathode during discharging. The anions intercalate at the graphite cathode. During charging, the anions pass back through the electrolyte and get deposited onto the metallic aluminum.

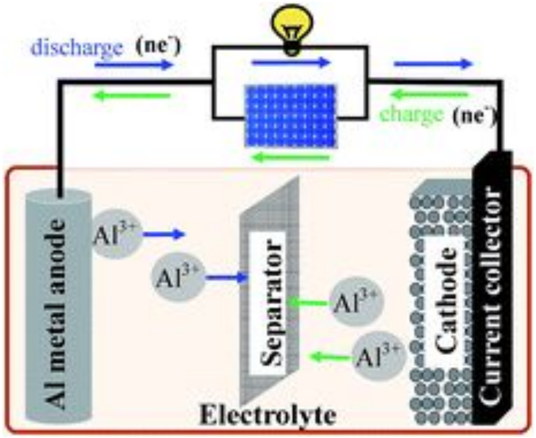


Figure: A simplified illustration of how an Al-ion battery works

Advantages

- Low cost
- Abundant
- Production scalability
- No dendritic formation during charging

Limitations

- Lack of oxidatively stable, inexpensive current collectors that can work in chloroaluminate ionic liquids
- The electrolyte fluid is very corrosive making conductive parts very vulnerable

Aluminum-Ion Batteries

Research & Technology

Two papers published by Swiss researchers in Advanced Materials in 2018 have come up with solutions to circumvent challenges in aluminum ion batteries.

1) Titanium nitride ceramic coating for protection

Researchers at the ETH Zurich in Switzerland have utilized a corrosion-resistant coating material, titanium nitride (TiN) ceramic, for usage in Al-ion batteries. TiN is a strong conductive material composed of abundant elements and is ideally suited for use as an Al chloride graphite battery ($AlCl_3$-GB) current collector owing to its **high oxidative stability** in the ionic liquid at potentials of up to 2.5 V versus Al^{3+}/Al.

The excellent stability of TiN coated materials enables batteries to attain a high coulombic efficiency of **99.5%**, a power density of **4500 W kg^{-1}**, and capability of at least **500 cycles**.

Further, TiN films can be deposited on stainless steel (SS) and flexible polyimide substrates for use in **coin and pouch cells**. The excellent stability of these TiN coated materials towards electrochemical oxidation enables these batteries to attain a high coulombic efficiency of 99.5%, the power density of 4500 W kg^{-1}, and capability of at least 500 cycles.

Aluminum-Ion Batteries

Research & Technology

Their results demonstrate that flexible current collectors could be fabricated by coating TiN by low cost, rapid, scalable methods such as **magnetron sputtering**. The cyclic voltammetry curve (CV) evaluations for TiN current collectors demonstrated stable values for TiN in $AlCl_3$ ionic liquid compared to molybdenum (Mo), tungsten (W) and glassy carbon (GC) ionic electrolytes. Nearly all metals including Au and Pt get corroded by $AlCl_3$-based ionic collectors. However, TiN current collectors exhibited **excellent corrosion resistance** even higher than the known alternatives including W, MO, and glassy carbon.

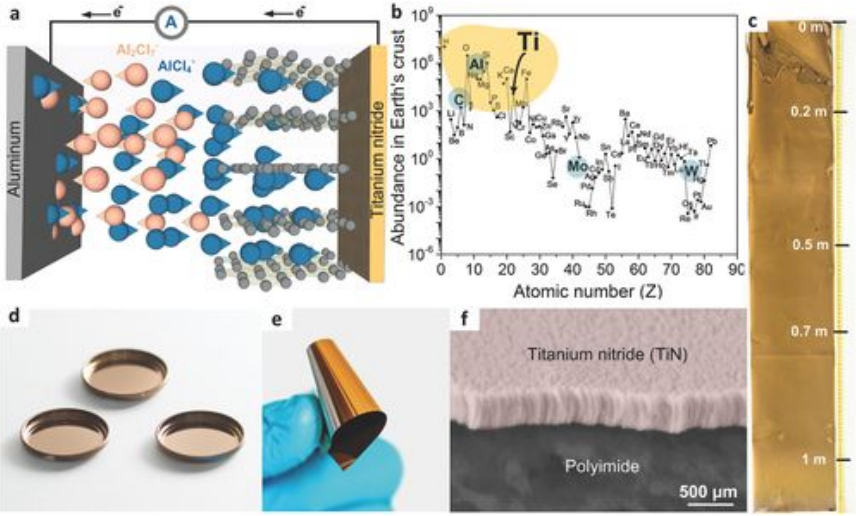


Figure: $AlCl_3$-GB with a TiN current collector. a) Schematic of the charging process. b) Element abundances in the Earth's crust (normalized per 106 atoms of Si) (the yellow region indicates rock-forming elements). Photographs of the c,e) TiN-coated (500 nm film thickness) polyimide and d) stainless steel substrates. f) Cross-sectional SEM image of TiN deposited on the polyimide substrate.

TiN current collector was found to outperform the common Al and SS current collectors particularly in Li (Na) bis(fluorosulfonyl)imide FSI-based electrolytes. Therefore, the usage of TiN is not limited to Al batteries. It could potentially be used as alternative current collectors for high voltage cathode materials in Mg, Na or Li-ion batteries. **The research demonstrates a promising step towards commercializing Al-ion batteries for use as an inexpensive and grid-level energy storage technology.**

Research & Technology

2) Polypyrenes as high-performance cathode material

Various forms of synthetic and natural graphite anodes have been tested in recent years for Al-ion batteries. The batteries typically use a graphite-based cathode. However, a large number of chloroaluminate anions in the graphite layers cause a distortion of the anion structure. These issues have prompted the search for alternative cathode materials.

Scientists from ETH Zurich have developed a new type of cathode based on **inexpensive pyrene polymers**. They have discovered that polypyrene and its derivative poly(nitropyrene-co-pyrene) can serve as highly flexible, adaptable and high capacity cathode materials for Al batteries.

The researchers tested a custom-made cell for electrochemical performance with Al anodes, tungsten cathodes cast with pyrene or polycyclic derivatives, in dried chloroaluminate ionic liquid (a mixture of [EMIm]Cl with$AlCl_3$, molar ratio 1.3:1).

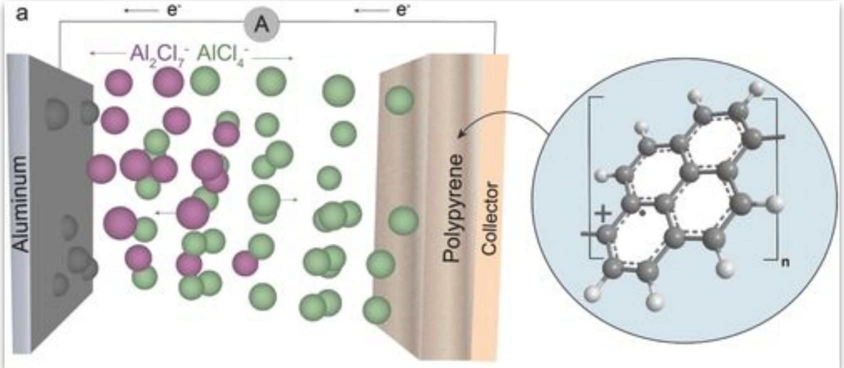


Figure: Schematic of the working principle of a rechargeable aluminum battery during charge with a polypyrene cathode and chloroaluminate ionic liquid.

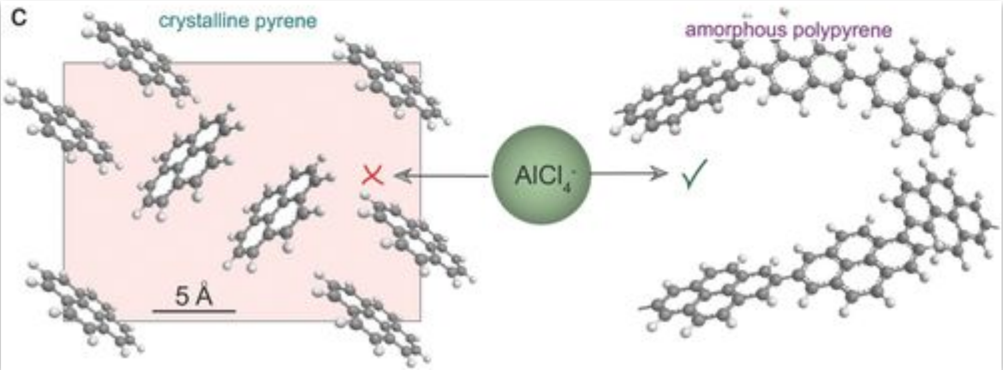
Aluminum-Ion Batteries

Research & Technology

The researchers found that a conductive polymer, known as polypyrene can store at least the same amount of energy as a graphite cathode in an Al-ion battery. During charging, the condensed aromatic rings of these polymers get oxidized accompanied by the uptake of aluminum tetrachloride anions ($AlCl_4$) from the chloroaluminate ionic liquid. Upon electroreduction of the polymer, $AlCl_4$ is released back to the ionic liquid.

The electrochemical properties of the polypyrene can be fine-tuned by appropriate chemical derivatization. The researchers have demonstrated the process by forming poly(nitropyrene-co-pyrene) which has a storage capacity of 100Ah g^{-1}, higher than the neat polypyrene (70mAh g^{-1}) or crystalline pyrene (20mAh g^{-1}) at a high discharge voltage of 1.7V. It demonstrates a higher energy efficiency of 86% and cyclic stability of at least 1000 cycles. Moreover, the material’s porosity can be influenced much easier compared to solid graphite.

Figure: Schematic representation of the structural differences between pyrene (crystalline, e.g., dense molecular packing) and polypyrene (amorphous, porous, and flexible), which impact their $AlCl^{4-}$ storage behavior.



Aluminum-Ion Batteries

Research & Technology

The ETH researchers also discovered that the disorderly arrangement of hydrocarbon polymer chains in polypyrene is required for a better battery. With a lot of space between the molecular chains, relatively large ions of the electrolyte can penetrate and charge the electrode material easily. As polymeric aromatic hydrocarbon compounds can offer vast possibilities in terms of compositional and structural tunability, low cost, high abundance, and production scalability, the research is a promising step for the development of rechargeable aluminum batteries.

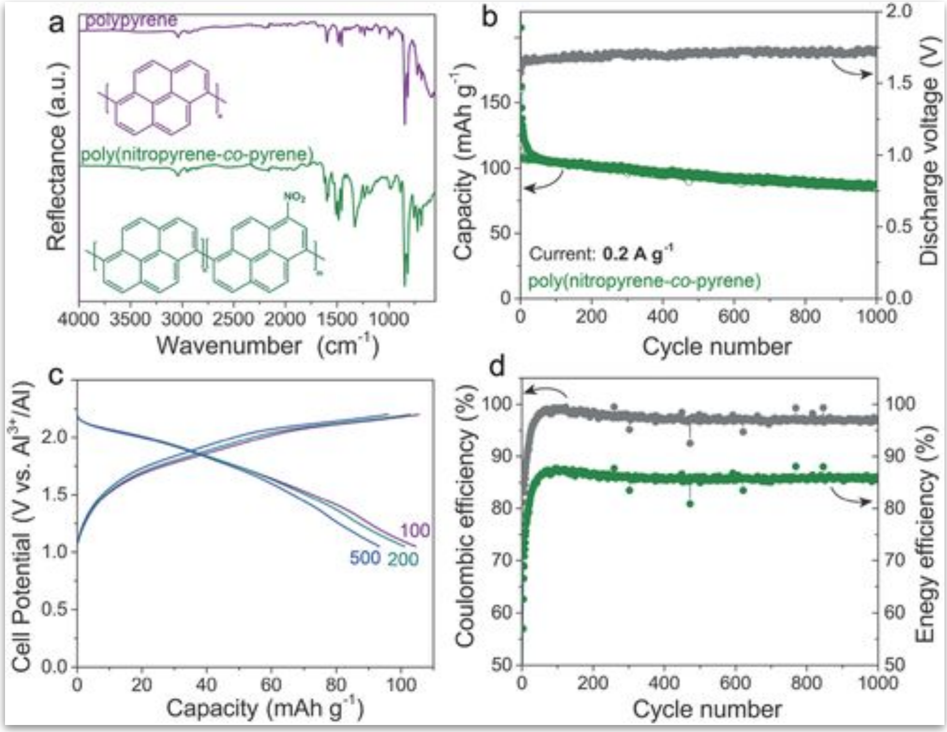


Figure: a) FTIR spectra of polypyrene (purple) and poly(nitropyrene-*co*-pyrene) (green). Electrochemical performance of aluminum batteries with poly(nitropyrene-*co*-pyrene) as the cathode material: b) capacity retention upon cycling and average discharge voltages, c) corresponding charge–discharge voltage curves for the 100th, 200th, and 500th cycles, and d) Coulombic and energy efficiencies. Cells were cycled at room temperature at a current density of 200 mA g^{-1} in the potential range of 1.05–2.2 V.

Aluminum-Ion Batteries

Commercial Developments

Al-ion batteries hold great promise, but are still far from commercialization.

Conclusion & Future Outlook

It is expected that future aluminum batteries could have a specific energy of around 1000 Wh/kg which is significantly higher than the 400 Wh/kg of a Li-ion battery. Aluminum batteries have the potential to offer more energy density, higher cycling rate while being compact and light at the same capacity than a Li-ion battery.

The efforts by the researchers is a promising start on further improvement of Al-ion batteries. Substantial work is needed particularly in understating the atomic details of the charge-storage and fading mechanisms, as well as optimization of the electrode, and mass loading for obtaining appropriate areal capacities before commercialization of Al-based batteries.

References

1. https://www.designnews.com/electronics-test/can-aluminum-take-us-beyond-lithium/44692193958697
2. https://www.ethz.ch/en/news-and-events/eth-news/news/2018/04/new-materials-for-sustainable-low-cost-batteries.html
3. https://onlinelibrary.wiley.com/doi/abs/10.1002/adma.201705644
4. https://onlinelibrary.wiley.com/doi/abs/10.1002/advs.201700712

Nickel-Zinc Batteries

Rechargeable Nickel-Zinc (Ni-Zn) batteries are highly safe, non-toxic and can compete with Li-ion batteries for energy storage systems and electric vehicles (EVs). Unlike other materials, both Ni and Zn can get recycled while maintaining their physical and chemical properties. Moreover, natural abundance of Zn makes Ni-Zn batteries cost-effective and environment friendly.

However, the low cycle life is an obstacle for the widespread commercialization of Ni-Zn batteries. These challenges arise due to the shape change, dendrite growth, passivation, and self-discharge of the zinc electrode owing to the zinc electrode dissolution into the solution during the charge or discharge process. Research attempts have been made to fix these issues by adding additives to the zinc electrode or electrolytes, changing separators, and designing 3-D zinc sponge anodes etc. However, the issue of zinc electrode dissolution still remains unresolved which limits the battery cycle-life. In 2018, researchers developed a breakthrough **in-situ cutting technique** to improve the performance of Ni-Zn batteries by solving the issue of Zn electrode dissolution.

Advantages	Limitations
Safe	Low cycle life
Non-toxic	Dendritic formation
Environment friendly	Zinc dissolution
Cost-effective	

Research & Technology

In a research published in Scientific Reports, scientists have demonstrated a novel graphene-ZnO hybrid electrode developed with in-situ cutting technique, which can directly cut graphene into **short nanoribbons**, and the strong interatomic interactions can anchor zinc atoms onto graphene surfaces. The scientists used SEM and TEM images to examine the microstructures of the new graphene-ZnO hybrid electrode (as seen in the adjacent figure).

This technique not only **fixes** the dissolution of zinc electrode but also **avoids** dendrite formation and increases the specific surface area of zinc to promote chemical reaction rate during the charge-discharge process. Further, the excellent electrical conductivity of graphene improves the speed of the charge-discharge process.

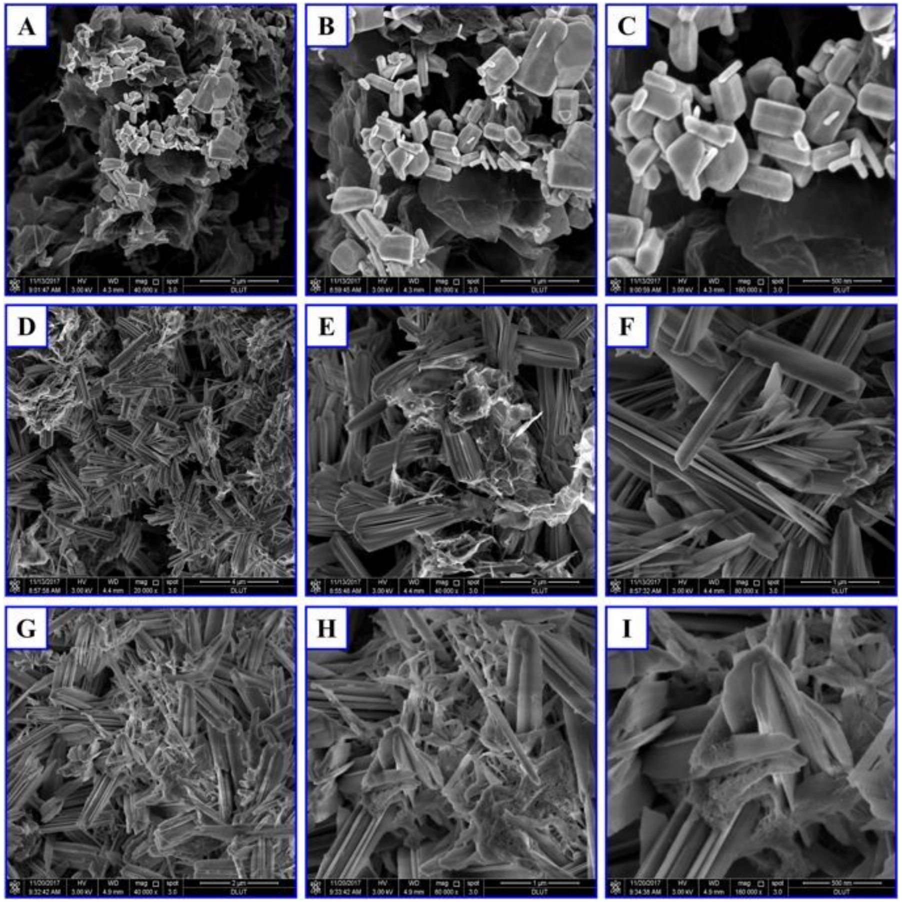


Figure: SEM images of the surface morphology of graphene-ZnO hybrid electrode (80.7 wt% ZnO) before cycling (A,B,C) and after 1000 cycles (D,E,F,G,H,I). (D,E,F) and (G,H,I) denote without and with the electrode washed by deionized water.

Nickel-Zinc Batteries

Research & Technology

The researchers performed a series of experiments and molecular dynamics simulations to measure the electrochemical performance of the newly designed rechargeable Ni-Zn battery. They found that discharge capacity of Ni-Zn batteries is as high as 2603 mAh/g^{-1} with a high electrochemical performance up to 10,000 test cycles. These results suggest that the cutting technique is very efficient in the electrochemical fields. The team claims that the issue of zinc electrode dissolution is thoroughly solved for a higher electrochemical performance of Ni-Zn batteries.

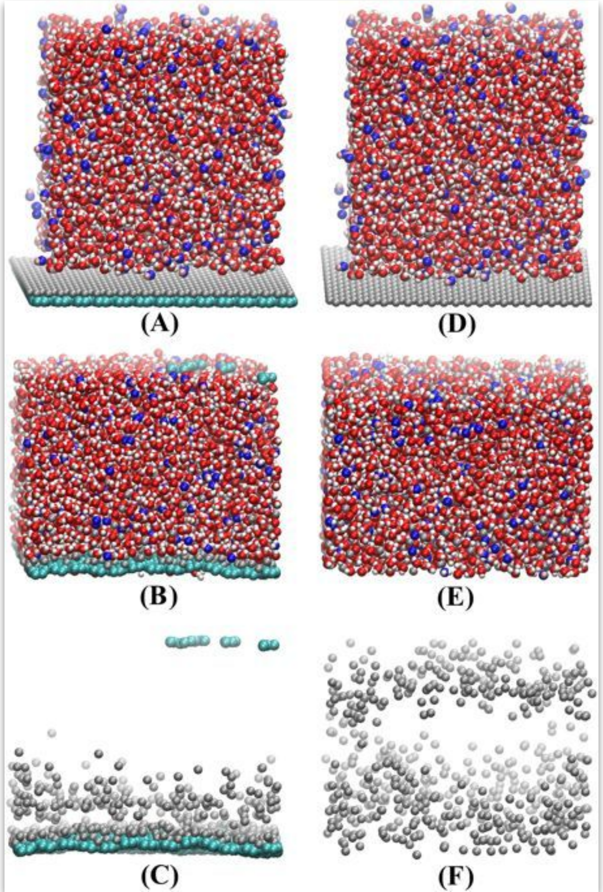


Figure: Initial (**A**), final (**B**) structure of the model system of graphene-Zn composite with OH$^-$solution and (**C**) the final structure of graphene and Zn. (**D**), (**E**) and (**F**) are the corresponding structure of the Zn with OH$^-$ solution

Commercial Developments

ZAF Energy Systems Inc. (ZAF), a developer of next-generation battery technologies received $600,000 investment from Missouri's Department of Economic Development Fund in June 2018. The company plans to use the investment to expand production and commercialize Ni-Zn batteries on a global scale.

The company has engineered **zincate nucleation additives** to maintain a stable zinc structure throughout the life-cycle of the electrode. They also add hydrogen suppressant additives to minimize drying out in the battery. ZAF's electrolyte is made of water, KOH and zinc stabilization additives. The novel electrolyte composition acts as a strand in a net encapsulating the zinc electrode. The positive electrode primarily made of NiOH and conductive aids is very robust and can be utilized over a broad range of current densities. Overall, ZAF has engineered various components in the Ni-Zn battery that has enabled them to bypass associated challenges.

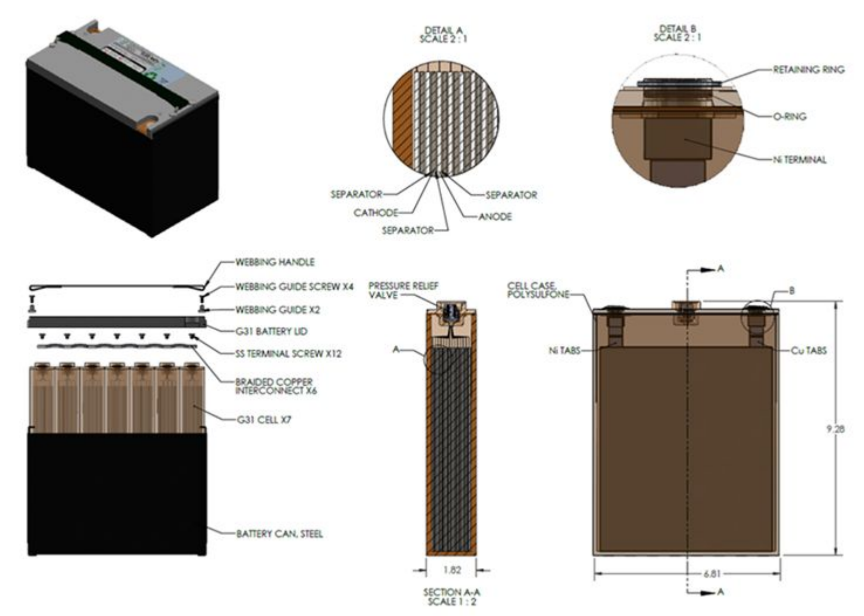


Figure: The core components of ZAF's battery system

Nickel-Zinc Batteries

Commercial Developments

A startup company, **ZincFive** has developed a **patented electrolyte solution** that gets rid of zinc solubility and dendritic formation. The company has improved and patented their positive and negative electrode composition which eliminates the toxic material. Ni-Zn batteries manufactured by ZincFive offer high power densities up to 3000W/kg and an enhanced cycling capability at a lower cost. The technology is safe and able to withstand all standard automotive tests.

The company launched a **modular uninterruptible power supply (UPS) system** for data centers, based on Ni-Zn batteries earlier in 2018. It is less hazardous than Pb-acid batteries and physically safer than Li-ion batteries. They deliver long life, require no maintenance and can operate at a wide temperature range. The ZincFive UPS model 48-3-208 uses Nickel-Zinc batteries alongside replaceable inverters designed by CE+T Power. QTS, an American cloud and colocation provider, is currently testing the modular UPS systems for adoption in their future applications.

Nickel-Zinc Batteries

Conclusion & Future Outlook

In conclusion, intense research efforts are on to improve the issues of Zn electrode dissolution, dendrite formation, and performance. Companies like ZAF Systems and ZincFive have used additives in the electrolyte formation that has improved the performance of Ni-Zn batteries for widespread commercialization. The batteries are low cost, safe, and possess good cycling capability over a wide temperature range for energy storage and other applications

References

1. https://www.nature.com/articles/s41598-018-23944-9
2. https://zafsys.com/zaf-energy-systems-receives-600000-investment/
3. https://zafsys.com/nizn-batteries/
4. https://www.zincfive.com/nickelzinc-overview/
5. https://www.datacenterdynamics.com/news/zincfive-set-to-launch-data-center-ups-with-nickel-zinc-batteries/
6. https://www.datacenterdynamics.com/news/qts-is-testing-ups-systems-with-nickel-zinc-battery-chemistry/

Potassium-Ion Batteries

In recent years, potassium-ion batteries (KIBs) have gained traction as low-cost alternatives to Li-ion technology for energy storage systems due to **high volumetric density**. However, a limited understanding of the underlying electrochemistry, lack of suitable electrode materials capable of inserting potassium (K) ions impedes the development of KIBs.

Due to the large size of the K ion, insertion of K into the electrode material is hindered leading to its low capacity and poor cycling performance. The research on KIBs is still in its nascent stage, with a limited understanding of the electrochemical mechanism of most electrode materials. Only a few cathode materials including Prussian blue, KMnFe $(CN)_4$, confined selenium (c-PAN-Se) and anode materials such as graphite/carbon, Sn_4P_3/C have been found to offer reasonable capacity. The cycling stability is still far from the commercial application.

Therefore, research is focusing on the identification of suitable electrode materials with high capacity, rate performance, and excellent cycling stability.

Advantages

- Low cost
- Potassium is abundant and easily extractable
- Similar electrochemical properties as Li-ion batteries
- High volumetric density

Limitations

- Lack of suitable electrode materials
- Limited understanding of underlying electrochemistry
- Low capacity
- Poor cycling performance

Potassium-Ion Batteries

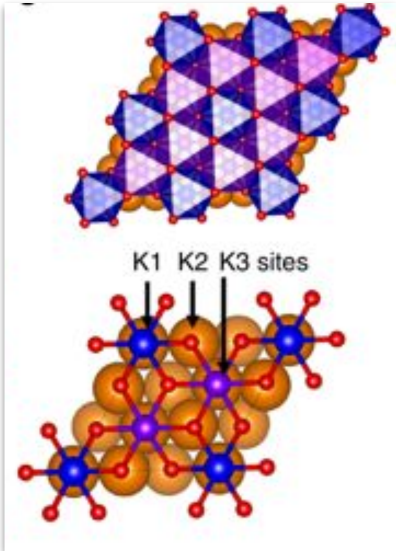
Research & Technology

1) Honeycomb-layered tellurates as high-voltage cathodes for K -ion batteries

A team of researchers explored the database for new layered cathode compounds and discovered a new family of honeycomb-layered compounds with a general formula of $K_2\mathrm{M}_2TeO_6$ (where M=Ni, Mg, Co, etc. or a combination of at least 2 transition metals). These honeycomb-structured potassium-based tellurate compounds offer suitable physical properties for high-voltage cathode materials. They show the capability of reversible insertion of K ions at high voltages of 4V in ionic liquids based on potassium bis(trifluorosulfonyl)imide, with excellent ionic conductivities.

Orthotellurate archetypes such as $K_2M_2TeO_6$ and related orthotellurates such as $K_2Ni_2TeO_6$ with high thermal stabilities can sustain successive K ion insertion and open a treasure-trove for high cathode materials. These layered honeycomb materials could also be extended to include a vast variety of stoichiometries that can enable synthesis of new honeycomb structured K-based materials with superior materials.

The study demonstrates that these layered tellurates are prime candidates for the advancement of high-energy KIBs. An ongoing research project is the design of Te-free compounds for reversible K-ion insertion at high voltages and capacities. Further, they are also testing Sb and Bi for application in KIBs.



A fragment of the magnetoactive honeycomb layers with three major K sites (K1, K2, and K3).

Potassium-Ion Batteries

Research & Technology

2) Few-layered composite anodes made by solution-triggered one-step shear exfoliation

Researchers at the University of Wollongong have demonstrated a high-performance KIB with a composite of few-layered antimony sulfide/carbon sheet (SBS/C) anode. The SBS/C anode was prepared via one-step high shear exfoliation in an ethanol/water solvent in a ratio of 2:1.

2D materials possess a highly accessible surface area and fast charge transfer kinetics which can help design suitable electrode materials. Antimony trisulfide (Sb_2S_3) has drawn extensive attention out of all the Sb-based anode materials due to a higher reversible capacity, and greater mechanical stability, cycling stability and rate performance. The researchers focused on designing a 2D Sb_2S_3 for improving the electrochemical behavior.

Bulk Sb_2S_3 crystal has a layered structure which makes the fabrication of 2D Sb_2S_3 possible. Layered bulk crystals can be exfoliated to obtain a monolayer and is an important technique to fabricate 2D materials for various applications. The researchers fabricated a few layered antimony sulfide/carbon sheet (SBS/C) anode via the high-shear exfoliation technique to boost the electrochemical performance of KIBs.

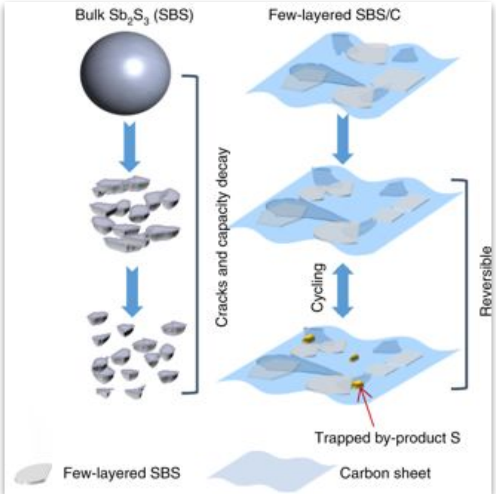


Figure: Schematic illustration of working mechanism of bulk SBS and few-layered SBS/C

Potassium-Ion Batteries

Research & Technology

Antimony sulfide with few-layered structure and withstand the volume expansion during potassiation and shortens the ion transport pathways, leading to a high rate capacity. **Carbon sheets** in the composite provide electrical conductivity and cycling stability by trapping the by-product, sulfur. The effects of exfoliation solvents on the fabrication of 2D- antimony sulfide/carbon was also investigated. The studies demonstrate that **water facilitates the exfoliation** by lower diffusion barrier along the direction of antimony sulfide while ethanol acts as a source of carbon for in situ carbonization.

The custom-made SBS/C composite anode delivers a specific capacity of **404 mA h g^{-1}** (after 200 cycles) and presents an outstanding rate capability with **76% capacity retention** at current densities from 50 to 500 mA g^{-1}. According to the final discharge products, the calculated theoretical capacity of SBS in KIBs is as high as 630 mA h g^{-1}. The strategy could be used for the fabrication of few-layered material/carbon composite for other layered crystals and exfoliated for composite fabrication with selected organic solvents to boost the performance of KIBs.

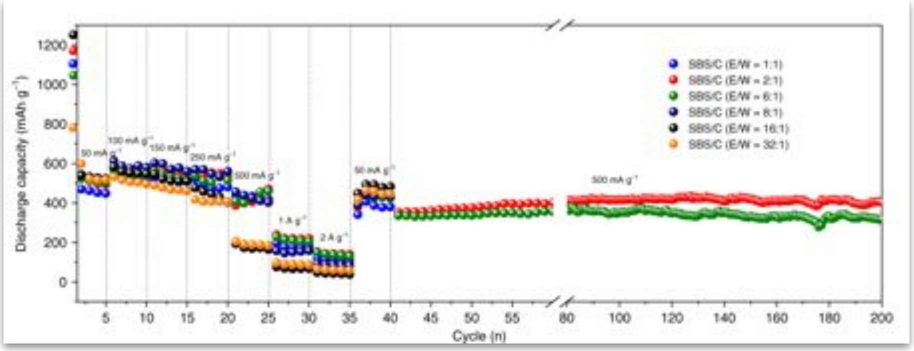


Figure: Rate capabilities of SBS/C electrodes exfoliated with different solvents (E/W = 1:1, E/W = 2:1, E/W = 6:1, E/W = 8:1, E/W = 16:1, E/W = 32:1) obtained at various charge and discharge current densities (at 50, 150, 300, 500, 1000, and 2000 mA g−1) and their cycling performance after rate testing at a current density of 500 mA g−1

Research & Technology

3) Porous network of bismuth (Bi) as anode for high-energy density KIBs

Not much research has been performed to optimize the synergy of electrode and electrolyte to boost the electrochemical performance of KIBs. However, recently researchers at Nankai University focused on the **synergistic combination of the electrolyte and electrode** to design a high-performance KIB. They developed a KIB with commercial Bi as the anode, and Prussian blue (PB) K0.72Fe[Fe(CN)6] as the cathode in combination with the dimethoxyethane (DME)-based electrolyte. The battery exhibits a remarkable capacity of **400 mAhg^{-1}**, high capacity retention of **86.5%** after 350 cycles and a high energy density of **108.1 Whkg^{-1}** at a power density of **566 Wkg^{-1}**.

The properties are favored by the unique K storage in the Bi anode in the DME-based electrolyte. The Bi develops into a 3D porous structure during electrode reactions. These are three two-phase reactions of Bi--KBi_2, KBi_2--K_3Bi_2, and K_3Bi_2--K_3Bi occurring at 1.15V, which enables fast K^+ kinetics and tolerance of the volume change of Bi permitting stable cycling. The porosity is linked to the strong chemical adsorption of DME molecules on Bi, leading to large energy density and high coulombic efficiency of 98.3%.

The excellent electrochemical performance of the full KIB is a promising start to realize the true potential of KIBs in large-scale electric energy storage applications.

Research & Technology

4) Metallic octahedral cobalt selenide threaded by N-doped carbon nanotubes framework (NCNF) as anode material for KIBs

Researchers have designed a metallic octahedral cobalt selenide ($CoSe_2$) threaded by NCNF for the first time as an advanced anode material for KIBs. The newly synthesized anode material allows for high-performance K storage. The NCNF network plays multiple roles, including conductivity, structural skeleton, restraining agglomeration, current collector, and capacity contribution.

The metallic $CoSe_2$ provides fast electrons transport and high theoretical capacity, which improves the performance of KIBs. Every octahedral $CoSe_2$ particle arranges along the carbon nanotubes in sequence, leaving zigzag void space among particles, which can accommodate the volume expansion and improve the structural stability during cycling. Moreover, the band gap of $CoSe_2$ is zero, which indicates its conductor property and benefits the rate performance of KIBs. The unique structure offers high rate performance and excellent cycling stability. The battery demonstrates promising abilities for practical applications in energy storage systems, especially for flexible and bendable devices.

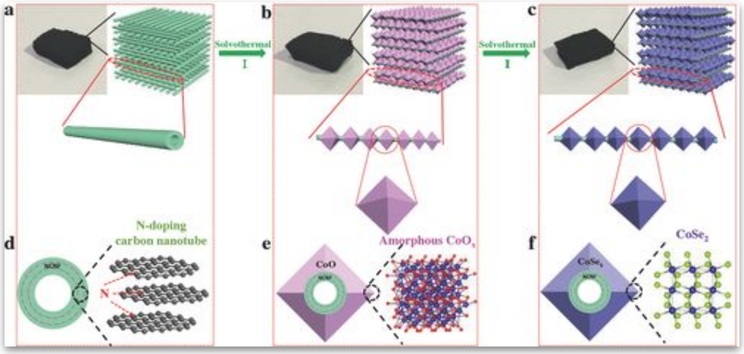


Figure: Fabrication of a) NCNF, b) NCNF@CoOx, and c) NCNF@CS. Cross section drawn and the corresponding structure of d) NCNF, e) NCNF@CoOx, and f) NCNF@CS.

Potassium-Ion Batteries

Research & Technology

5) High performance Red P nanoparticles integrated in a 3D porous carbon nanosheet (CN) network

Researchers for the first time tested Red P as an anode for KIBs by uniformly anchoring red P nanoparticles in a 3D porous CN framework. The novel red P@CN nanocomposite offers fast K ion kinetics, interconnected electron conductive pathway, large active surface, and a fast charge/discharge reaction leading to a superior performance. The battery with the red P@CN nanocomposite has a high reversible capacity of 655 mA h g^{-1} and a superior rate capability with a high capacity retention of 323.7 mA h g^{-1} at a current density of 2000 mA g^{-1}, which by **far surpasses all known anode materials reported for KIBs**.

The researchers also investigated the electrochemical reaction mechanism between red P and K using galvanostatic intermittent titration technique (GITT), TEM, and theoretical calculations. The one-electron reaction of $P + K^+ + e^- \rightarrow KP$ was proposed to be responsible for the K storage in red P, corresponding to a theoretical capacity of 843 mA h g^{-1}.

The study offers a fundamental understanding of the potassium storage mechanism of red P and suggests the design of high-performance red P anodes for KIBs.

Potassium-Ion Batteries

Commercial Developments

Currently, the only company that successfully marketed the K battery portable media player as a high-energy device is a Chinese company, Starsway Electronics. There is a lot of commercial interest in KIBs. The research groups are seeking commercial investments to commercialize the KIBs.

Conclusion & Future Outlook

There have been a lot of recent breakthroughs to improve the electrochemical performance of Potassium-ion batteries. Research efforts have focused on optimizing the battery design by applying techniques to improve electrodes and synergy between electrodes and the electrolyte solutions. The hurdle of the host substrates being incapable of intercalating K ions has circumvented by the unique and novel approaches by various research groups. A high-performance KIB with high rate performance, long-life, cycling, and coulombic efficiency with the ongoing research efforts is a promising step towards attracting industrial investments.

References

1. https://www.nature.com/articles/s41467-018-05786-1
2. https://www.nature.com/articles/s41467-018-06343-6#Sec7
3. https://onlinelibrary.wiley.com/doi/abs/10.1002/anie.201801389
4. https://onlinelibrary.wiley.com/doi/full/10.1002/advs.201800782
5. https://onlinelibrary.wiley.com/doi/abs/10.1002/smll.201802140

Salt-Water Batteries

Water is found everywhere, is inexpensive, non-flammable and can conduct ions. Therefore, water could be used to form inexpensive rechargeable batteries for the future. However, water is chemically stable up to a voltage of 1.23 volts, which is about three times less than existing lithium-ion battery. These limitations make water less suited for applications such as EV. However, water-based batteries would be useful for stationary power storage applications. Researchers at the Swiss Materials Testing and Research Institute (Empa) have used a special salt (sodium bis (fluoro sulfonyl) imide) FSI, to solve the problem.

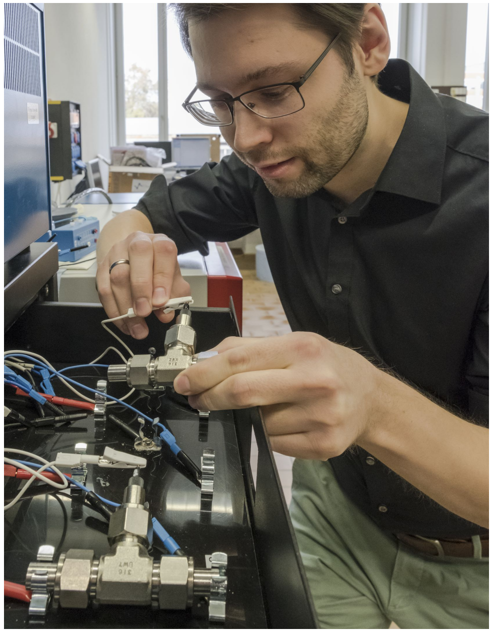


Figure: Empa researcher connecting a test cell to the charger with the concentrated saline solution. Photo: Empa

Advantages

- Inexpensive
- Non-toxic
- Safe
- Long life

Limitations

- Low performance
- Limited efficiency

Salt-Water Batteries

Research & Technology

1) Empa's water-based rechargeable battery

Researchers at the Swiss Materials Testing and Research Institute (Empa) used a special salt called sodium bis(fluorosulfonyl)imide (FSI). This salt is extremely soluble in water. The salt-containing liquid has all the water molecules concentrated around the sodium cations in a hydrate shell. Hardly any unbound water molecules are present, making it a saline solution without free or excess water. The researchers discovered that this salt solution has an exceptional electrochemical stability of up to 2.6 V, which is twice as high as other aqueous electrolytes. The discovery could lead to inexpensive, low-cost and safe battery cells as sodium FSI cells can be constructed with more safety and ease than lithium-ion batteries.

Initial results in the laboratory have already shown promising results with the battery. The system can withstand a series of charge and discharge systems. Until now, the researchers have tested the battery's anodes and cathodes separately - against a standard electrode as a partner. The next step would be to combine the two-half cells into one battery for additional testing. The innovation would take the group one step closer to using the technology commercially.

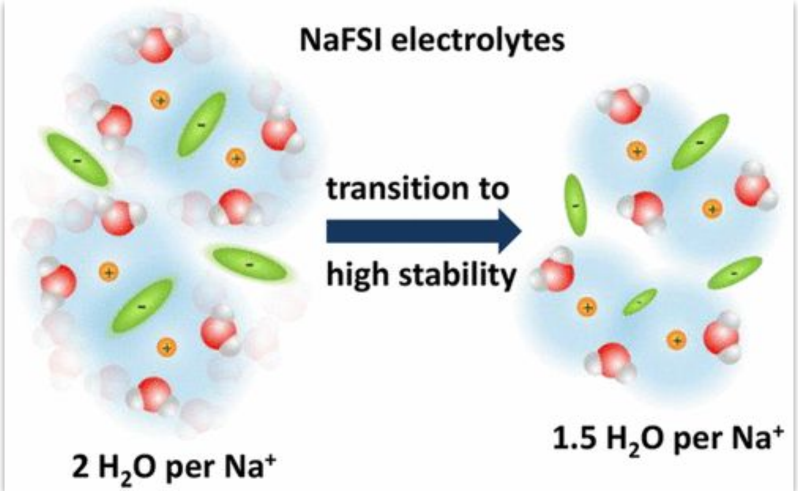


Figure: Principle of high-voltage rechargeable aqueous salt-water batteries

Salt-Water Batteries

Research & Technology

2) Stanford's rechargeable saltwater battery innovation

Stanford researchers developed a low cost, durable saltwater battery for solar and wind energy storage. The new saltwater batteries are easy to develop as they only require manganese sulfate, water, and electrodes for the catalytic reactions. A renewable grid needs back up batteries that could store excess power for redistribution when the solar panels and wind turbines are not working. Stanford's rechargeable salt-water battery innovation can solve these issues.

The researchers induced a reversible electron exchange between water and manganese sulfate, an inexpensive industrial salt used to produce dry-cell batteries, fertilizers, paper, and other products. They mimicked the conditions of a wind or solar energy feeding power to the battery by connecting a power source to the prototype. The electrons flowing in reacted with the manganese sulfate dissolved in the water to leave MnO_2 attached to the electrodes, with the excess electrons released as hydrogen gas. Therefore, this reversible chemical reaction stores electrons in the form of hydrogen gas for future use.

The prototype can be scaled up, has a stable performance up to 10000 cycles and a life span superior to 10 years.

Salt-Water Batteries

Research & Technology

To further investigate the rechargeability of the prototype, the team re-attached the power-source to the depleted prototype. Their results demonstrated the clung MnO_2 on the electrode could combine with water and replenish manganese sulfate salt. Therefore, electrons became surplus with the salt and the excess power released as hydrogen gas. These results demonstrate the suitability of the battery for grid-scale applications.

The prototype manganese-hydrogen battery is mere 3 inches tall and generates only 20 milliwatt hours of electricity. However, the researchers are currently optimizing to scale up the technology to an industrial-grade system that could undergo charge/discharge cycles of up to 10000 times, for the development of a grid- scale battery with a long life.

Although the design and the materials still need further development, the breakthrough battery prototype as reported in the Nature Energy on April 30, 2018, demonstrates a promising potential to a low-cost, long-lasting, utility-scale batteries. Currently, the researchers are focusing on using platinum and potential cheap materials as a catalyst for the chemical reactions at the electrode to make an efficient recharge process. **The team is in the process of patenting the technology before widespread commercialization.**

Salt-Water Batteries

Commercial Developments

Salt-water batteries have generated widespread research in Industry due to its safety, non-toxicity, simplicity, long-life and a cost-effective system of manufacturing.

The American company, **Aquion Energy** have secured an investment of $33 million early in 2018 to expand sustainable salt-water batteries. The battery is composed of a salt water electrolyte, manganese oxide cathode, carbon titanium phosphate composite anode, and a synthetic cotton separator. The battery uses non-corrosive intercalation reactions at the anode and cathode. By using these simple materials, Aquion is working on making the batteries low-priced enough to disrupt the grid battery market.

Another company at the forefront of the salt-water battery is Austria-based **BlueSky Energy**. They use Aquion's saltwater technology and Benan Energy's new generation of saltwater technology from China. They offer saltwater based residential solar storage.

Salt-Water Batteries

Conclusion & Future Outlook

When it comes to weight and power density, salt-water batteries suffer from lower performance, which makes them unfit for EVs. Currently, their application is limited to stationary storage systems. Nonetheless, they offer several advantages including safety, non-toxicity and low cost.

References

1. https://phys.org/news/2018-01-inexpensive-stablethe-salt-battery.html
2. http://www.hannovermesse.de/en/news/two-half-cell-salt-water-batteries-already-work-67200.xhtml
3. https://www.empa.ch/web/s604/salt-water-battery
4. https://pubs.acs.org/doi/ipdf/10.1021/acsenergylett.7b00623
5. https://www.nature.com/articles/s41560-018-0147-7
6. https://news.stanford.edu/2018/04/30/new-water-based-battery-offers-large-scale-energy-storage/
7. http://aquionenergy.com/technology/deep-cycle-battery/
8. https://www.betterworldsolutions.eu/saltwater-battery-gets-33-mln/
9. http://www.bluesky-energy.eu/en/bluesky-energy/
10. https://www.pv-magazine.com/2018/05/10/blue-sky-energy-offers-saltwater-based-residential-solar-storage/

Paper-Polymer Biobatteries

The dramatic increase in electronic waste has tremendous effects on the environment and public health. Energy supplying devices are the most problematic due to their high toxicity and reactivity. Paper-based batteries have emerged as a simple, biodegradable, inexpensive potential solution for disposable electronics and decrease of obsolete power devices. Among these, paper-based microbial biobatteries are of special interest by being cost effective, environmentally friendly and self sustainable. Also, this is a potential technology to provide energy availability to limited energy resource settings. However, the main challenge to overcome is still the low performance of such devices. One of the highlights of the paper-based biobattery is the potential application in **biosensors**, that by being inexpensive, disposable, flexible and with a high surface area can be an alternative to commercial batteries.

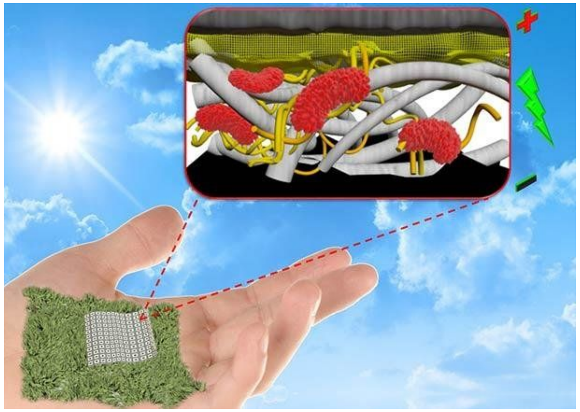


Figure: Schematic illustration of the paper-polymer biobattery. Image credits: Seokheun Choi

Advantages

- Cost-effective
- Environmentally friendly
- Biodegradable
- Flexible

Limitations

- Low performance
- Short shelf life

Paper-Polymer Biobatteries

Research & Technology

Seokheun Choi and a team of researchers, at the State University of New York-Binghamton, have developed a high-performance microbial battery engineered from a biodegradable paper-polymer substrate. The hybrid paper-polymer microbial fuel cells are biodegradable without the need of additional conditions or microorganisms, and compared to other paper biobatteries, show a **higher power to cost ratio**.

Freeze-dried exoelectrogens or electric bacteria (bacteria that export electrons as a byproduct of respiration) were embedded in pores in paper. Choi incorporated a biodegradable polymer mixture of poly (amic) acid and poly (pyromellitic dianhydride-p-phenylenediamine) in the paper to improve electrical performance by creating a conductive anodic reservoir that facilitated more electrons to be harvested from the bacteria. Previously reported microbial fuel cells allowed electrons to be harvested only from bacteria close to the anode.

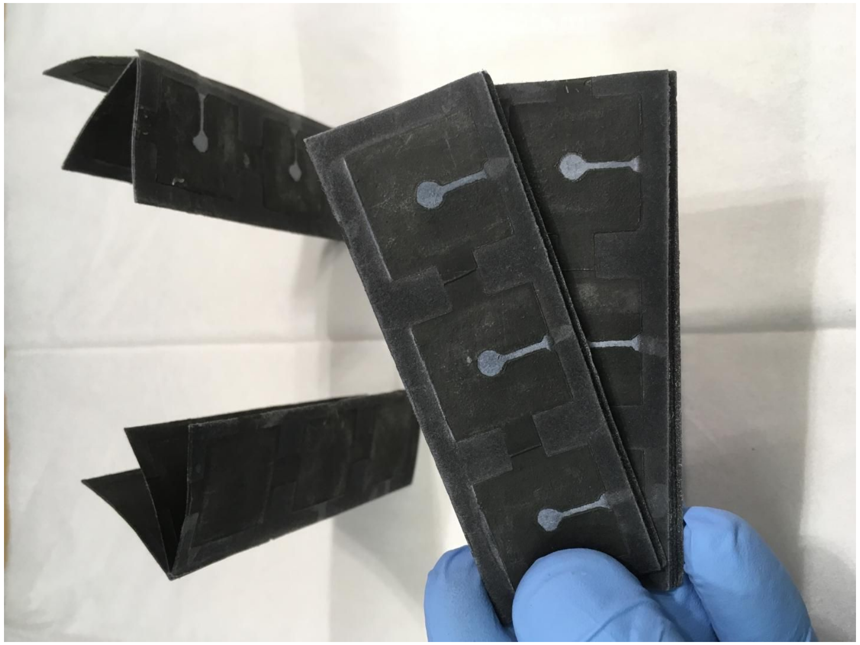


Figure: Researchers harnessed bacteria to power these paper batteries. Image credits: Seokheun Choi

Paper-Polymer Biobatteries

Research & Technology

By fabricating multiple battery cells on a single sheet of paper and folding the paper, seven battery cells connected in series were obtained that produced about 88 microwatts. Two of these battery packs were able to power a calculator and three powered a red light-emitting diode. Even though any organic liquid can serve as an energy source for the bacteria, the researchers included a pouch of cell-culture medium that could be released manually to rehydrate the bacteria and serve as an energy source.

The battery has been engineered to minimize oxygen penetration by tightly attaching the bacteria to the paper fibers, which leads to the formation of a multilayered biofilm. Currently, the paper biobattery has a shelf life of 4 weeks. Improvements on the freeze dried cell survival and power performance are under development.

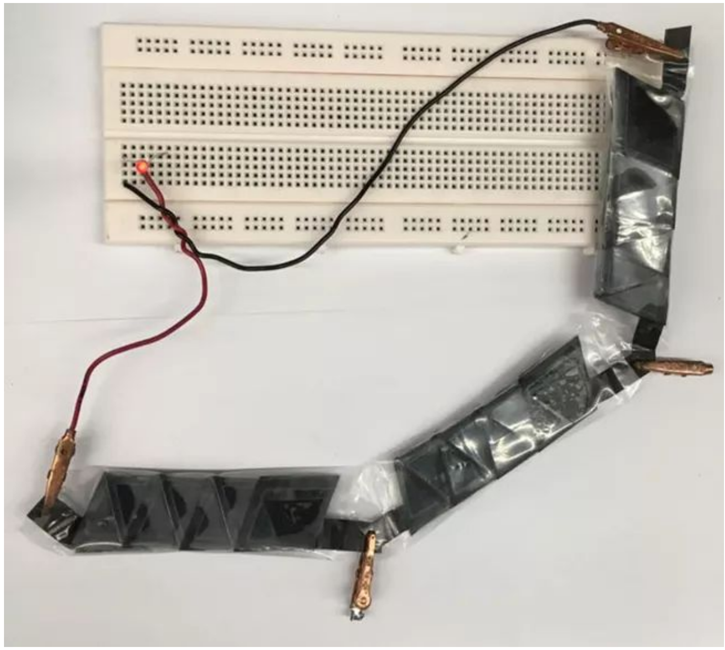


Figure: A group of folded batteries can power a paper-based electronic device. Seokheun Choi/Binghamton University, [CC BY-ND]

Paper-Polymer Biobatteries

Commercial Development

The technology is currently under patent application and Seokheun Choi is looking for industry partners to bring this innovation to commercialization.

Conclusion & Future Outlook

Paper-polymer biobatteries could be revolutionary for the future electronic devices and biosensors. The versatility such batteries offer in terms of the possibility of incorporating other materials such as metals, semiconductors, and nanoparticles and production of the paper/polymer/bacteria blend via various manufacturing process (roll-to-roll printing, screen printing, even painting directly on paper) will add further properties and capabilities and open the door to a new generation of electronics.

References

1. https://www.eurekalert.org/pub_releases/2018-08/acs-apb071718.php
2. https://onlinelibrary.wiley.com/doi/full/10.1002/adsu.201800041
3. https://theconversation.com/paper-based-electronics-could-fold-biodegrade-and-be-the-basis-for-the-next-generation-of-devices-102759
4. https://cen.acs.org/analytical-chemistry/Freeze-drying-extends-paper-biobatteriesshelf/96/web/2018/08

Magnesium Batteries

Li-ion batteries are approaching their energy density storage limits, and new battery systems are needed with high energy density at low cost of manufacture. Magnesium (Mg)-based batteries are potentially more advantageous than Li-ion batteries containing, in theory, almost double energy density capacity. Additionally, Mg is a more abundant material and cost effective than Li and also has the potential to deliver two times more energy since it releases two electrons. Also, Mg-metal based batteries do not experience the growth of dendrites (crystals responsible for short circuits with consequent overheating and fire) which is crucial for safer battery systems. However, the reversible chemistry strategy applied to Li-ion systems can not be applied to Mg-based batteries. In the case of Mg-metal system, a reversible reaction requires the use of a corrosive electrolyte, that produces a layer on the Mg electrode creating a barrier for Mg^{2+} ions and thus blocking the recharging of the battery.

A magnesium-based material developed that could allow for solid-state magnesium-ion batteries (Credit: Leiem/CC-BY-SA-4.0)

Advantages

- High energy density capacity
- Cost-effective
- No dendrite formation

Limitations

- Corrosive electrolyte
- Non-rechargeable

Magnesium Batteries

Research & Technology

1) Rechargeable Mg-metal batteries

A new rechargeable non-aqueous Mg-metal battery was developed by scientists at the Department of Energy’s National Renewable Energy Laboratory (NREL). The innovative strategy consisted of creating an artificial Mg^{2+} conductive solid interphase on the Mg anode surface from polyacrylonitrile and magnesium-ion salt. This interface protects the surface of the Mg anode, enabling the reversible cycling of a Mg/V_2O_5 full-cell in a water-containing, carbonate-based electrolyte, contributing to a significant improvement of the Mg-metal battery performance.

For the first time a prototype of a rechargeable Mg-metal battery is presented. The prototype with the protected anode demonstrated higher energy production than the prototype without anode protection working continuously after several cycles. New potential materials can in future be explored based on this approach, opening the possibilities towards the development of alternative multivalent-cation batteries. The work was developed by Chunmei Ban team in NREL’s Materials Science department.

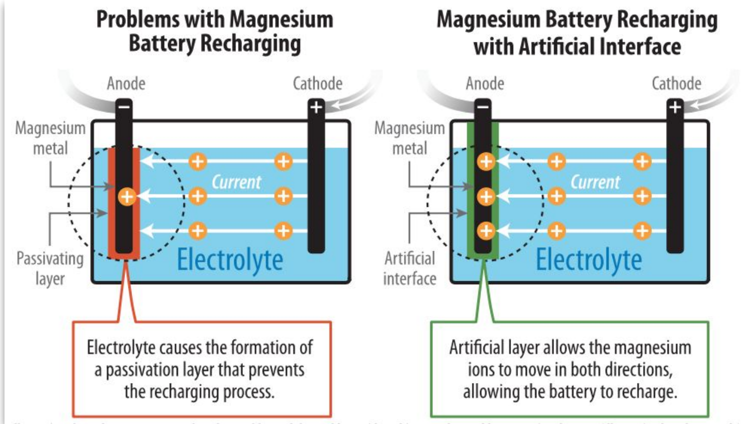


Figure: Illustration shows how NREL researchers have addressed the problem with making a rechargeable magnesium battery. (Illustration by John Frenzl / NREL)

Magnesium Batteries

Research & Technology

2) Solid state Mg-ion batteries (High magnesium mobility in ternary spinel chalcogenides)

A collaboration between Berkeley Lab, MIT and Argonne National Laboratory has led to the development of a solid-state material that appears to be one of the fastest conductors of Mg-ions. Previous studies worked on developing better liquid electrolytes, however due to the corrosive tendency of such, researchers looked into making a solid-state electrolyte. They achieved high Mg^{2+} mobility in solids by tuning the crystal structure and chemistry. With combining ab initio calculations, synchrotron X-ray diffraction (XRD), electrochemical impedance spectroscopy and solid-state nuclear magnetic resonance (SS-NMR), the researchers demonstrated that facile Mg^{2+} conduction at room temperature can be achieved in close-packed frameworks, particularly in the magnesium scandium selenide spinel ($MgSc_2Se_4$).

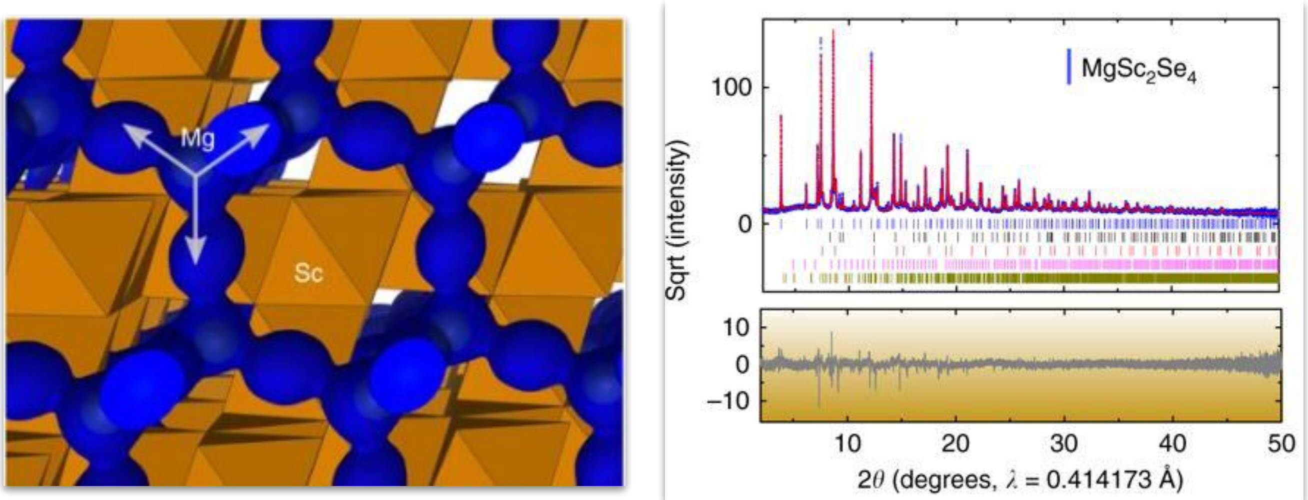


Figure: (Left) Mg probability density in $MgSc_2Se_4$ at 900 K obtained from ab initio molecular dynamic simulations (AIMDs). (Right) Rietveld refinement of the synchrotron XRD pattern for MgSc2Se4. The square root of the intensity is plotted on the y-axis.

Magnesium Batteries

Commercial Development

Further testing and research is needed before rechargeable Mg batteries or Mg solid state batteries enter commercialization.

Conclusion & Future Outlook

Magnesium has the potential to replace lithium-ion batteries given the advantages of double the energy and lower risk of overheating (due to no dendrite formation). However, an ideal Mg-based battery technology is still to be achieved. On going research and developments as those seen here will propel development much closer to commercialization in the not so far future.

References

1. https://www.nrel.gov/news/press/2018/nrel-research-overcomes-major-technical-obstacles-in-magnesium-metal-batteries.html
2. https://www.nature.com/articles/s41557-018-0019-6
3. https://www.nature.com/articles/s41467-017-01772-1

About the Authors

Sofiane Boukhalfa, PhD

PreScouter

Professional Summary: Sofiane leads the high-tech, aerospace and defense, and finance verticals at PreScouter. Sofiane earned his B.S. in Materials Science and Engineering from The University of Illinois at Urbana-Champaign, and his Ph.D. in Materials Science and Engineering from the Georgia Institute of Technology, where his research focused on nanotechnology and energy storage. Since graduating from Georgia Tech, he has worked as an emerging technology and business strategy consultant at several firms and for his own clients.

About the Authors

Navneeta Kaul, PhD

University of Denver, USA

Professional Summary: Navneeta Kaul recently completed her PhD in Biology at the University of Denver in Colorado. After earning an engineering degree in Biotechnology, her passion for cutting-edge biological research motivated her to pursue her Master's at the University of Arizona in Tucson. At the University of Denver, she studied the biological mechanism behind Fragile X syndrome, an autism spectrum disorder affecting nearly 1.3 million adults in the United States.

Research Background: Navneeta graduated with a PhD in Biology from the University of Denver in August 2018. The focus of her research was to understand the mechanism of local protein synthesis at the synapse which is important for memory formation in vertebrates. She has experience in using biochemical and molecular biology techniques like cloning, PCR, real-time PCR, western blotting, immunoprecipitation, live cell and fixed cell imaging.

Scientific Interests: Biotechnology, Life science consulting, Scientific communication, Microscopy, Engineering, Market research analysis, Business development.

About the Authors

Miriam Sousa, PhD

University of Lisbon, Portugal

Professional Summary: Miriam earned her PhD in Biotechnology and Biosciences (October 2018) under the topic “Nanofiber scaffold systems for neural stem cell culture applications” at Instituto Superior Técnico – Universidade de Lisboa (IST/UL). Her main research is focused on the effect of bio-functionalized nanofiber scaffolds on neural stem cells fate, in static and dynamic cultures, using mouse and human cell models, and also on the development of stirred systems with integrated scaffolds for NSC culture studies. She is interested in smart materials engineering (nanostructured, biocompatible and polymeric membranes) for biological or industrial applications.

Research Background: Bioengineering, Biotechnology, Stem cells, Physical-Chemistry, Chemical/Material Engineering (biocompatible materials, polymeric membranes), Nanotechnology.

About PreScouter

PreScouter provides customized research and analysis

PreScouter helps clients gain competitive advantage by providing customized global research. We act as an extension to your in-house research and business data teams in order to provide you with a holistic view of trends, technologies, and markets.

Our model leverages a network of 2,000+ advanced degree researchers at tier 1 institutions across the globe to tap into information from small businesses, national labs, markets, universities, patents, startups, and entrepreneurs.

Clients rely on us for:

Innovation Discovery

PreScouter provides clients with a constant flow of high-value opportunities and ideas by keeping you up to date on new and emerging technologies and businesses.

Privileged Information

PreScouter interviews innovators to uncover emerging trends and non-public information.

Customized Insights

PreScouter finds and makes sense of technology and market information in order to help you make informed decisions.