



**SOLAR SAVINGS**

# STORY ON GREEN ENERGY STORAGE

SUCCESS STORIES ON MATERIALS FOR ENERGY STORAGE







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Dr. Ranjith Krishna Pai received the Ph.D. degree in Natural Sciences, from Dr. Othmar Marti's Group, Ulm University, Germany, in 2005. He is currently Scientist 'E' / Director of Technology Mission Division of Department of Science and Technology responsible for research, development and innovation activities in Clean Energy domain.

He has represented India in numerous multi lateral event and has articulated national and international endeavors in energy domains. From 2006 to 2007, he was a Postdoctoral Researcher at University of Chile, Santiago, aworking on Genetic engineering of a novel protein-nanoparticle hybrid system with great potential for bio sensing applications. 2007 to 2009, he spent two years as a Post-Doctoral Scientist at Stockholm University, Stockholm, Sweden, working on synthesis of nanostructured hybrid materials and Characterization of nonlinear optical nanomaterial. From 2009 to 2011, he was a Research Scientist at CFN, Brookhaven National Laboratory, New York, USA, working on photo fabrication of donor- acceptor antenna system for solar energy harvesting, development of bio sensing platforms based on bio-inorganic scaffolds with single molecule/particle sensitivity, fabrication of transparent organic thin-film for use in organic photovoltaic cells. After spending 2 years 5 months at BNL, New York, USA, he spent another 2 years 4 months (2011-2013) as a Research Scientist at INL - International Iberian Nanotechnology Laboratory, Braga, Portugal. His research at INL involved development of transparent conjugated polymer films for capturing solar energy, organic thin-film solar cells based on conjugated polymers and fullerene derivative, hybrid organic/inorganic nanomaterial and synthesis and fundamental study of conjugated polymers, solar device fabrication and electrical and photochemical device measurements. From 2013 to 2015, he was an Associate Professor and Group leader at Nanostructured Hybrid Functional Materials & Devices, Jain University, Bangalore, India.

He published several high impact scientific papers, authored three book chapters and gave several invited lectures at international conferences. Previously served as an Associate Editor of a Journal "Nano tools & Nano machines" and a Guest Editor of International Journal of Polymer Science. His research interest includes energy conversion technologies, including low cost photovoltaic (Organic, and hybrid solar cells) and electrical energy storage (batteries and supercapacitors), synthesis of semiconducting polymers and polymer nanostructures and their application to organic transistors, solar cells, light emitting diodes and other photonic applications, synthesis, characterizations and applications of carbon and inorganic nanotubes, Modeling of the electronic properties of nanostructured semiconductors.



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Dr. Anita, an alum of Indian Institute of Technology, Delhi with Ph.D in Engineering and also alum of MANIT Bhopal for PG and NIT Raipur at undergraduate level, possesses over 25 years+ of professional experience in Management of various initiatives of Government of India on Innovation, Entrepreneurship, Startups and Incubation at premier Technology Institutes with Pan India coverage.

She played a pivotal role in horizontal and vertical growth of innovation, entrepreneurship and startups in the country and have been a lead catalyst in establishing over 155 technology business incubators at Institutions of Excellence including IITs, IIMs, NITs, IISERs, CSIR labs and leading public and private universities and institutions.

She lead various first of its kind initiatives on advancing innovation value chain. This includes promoting women entrepreneurship, innovation to prototype or support, seed support to startups, accelerator, Centre for Excellence in Incubation, capacity building and international market access program for Startups through bilateral and multilateral partnership programs. Dr. Anita is a member of various National Committees on Innovation, Startups and Incubation steered by DPIIT, MeitY, Office of PSA, MSME, Department of Defense Production, MoD, AICTE, MoE, DBT, AIM- NITI Aayog etc. She ia a demonstrated leader in propelling innovations of excellence and innovations of relevance driven with rich blend of experience, passion, commitment with quality outcomes and impact.





भारत शासन

डॉ. रेणु स्वरूप  
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एक कदम स्वच्छता की ओर



सचिव  
भारत सरकार  
विज्ञान एवं प्रौद्योगिकी मंत्रालय  
विज्ञान एवं प्रौद्योगिकी विभाग

Secretary  
Government Of India  
Ministry of Science and Technology  
Department of Science and Technology



10<sup>th</sup> September 2021

### FOREWORD

Materials discovery and development crosscut the entire energy technology portfolio, from energy generation and storage to delivery and end use. Materials are the foundation of every clean energy innovation: advanced batteries, solar cells, lowenergy semiconductors, thermal storage, coatings, and catalysts for the conversion, capture, and use of carbon dioxide. In short, new materials constitute one of the cornerstones for the global transition to a low-carbon future. The process of discovering and developing new materials currently entails considerable time, effort, and expense. Each newly discovered molecule is run through simulation, synthesis, and characterization, with synthetic procedures taking from 10 to 20 years at a very high cost. Materials discovery and development, however, are at the cusp of a transformational change that could reduce the time to design, optimize, and discover new materials by at least 10 times, cutting it down to one or two years.

Recognizing the challenges and opportunities associated with materials discovery, Department of Science & Technology under its Clean Energy Research Initiative (CERI) mounted a thematic Research and Technology Programme on energy materials. Materials for Energy Storage (MES) programme has supported R&D activities aimed at innovative materials for energy storage and to build energy storage device with enhanced output for multifunctional applications. A set of seventy seven projects have been supported under this program so far across three important areas such as Battery, Supercapacitor and Thermal Energy Storage. All these projects are currently in different stages of implementation.

These success stories on Materials for Energy Storage (MES) focus on 14 successful projects under Materials for Energy Storage (MES) programme that are expected to reach pilot plant/ application level demonstration in coming months. I hope these success stories on MES will enable researchers, stakeholders and general audience to know about the scientific developments in energy storage that can be scaled up according to national needs and priorities in the near future.

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# 1

## Vanadium Redox Flow Battery based charging station for portable electronic devices

Project Reference No. DST/TMD/MES/2K18/54

IIT Delhi's Sustainable Environment Research Lab (SERL) at the Department of Chemical Engineering is actively working on Vanadium Redox Flow Battery (VRFB) technology. Recently, a VRFB based charging station, especially designed under Smart Campus Initiative of the Institute, was inaugurated on the campus.

The charging station is designed to charge portable electronic devices such as mobile phones, laptops, tablets, and power banks. Along with the IIT Delhi community, visitors to the Institute will be able to utilise the VRFB based charging facility.

Dr. Anil Verma, Professor at Chemical Engineering Department, IIT Delhi said that the research group led by him developed the 2nd generation prototype in the SERL so that the technological and scientific contribution in the form of an environmental friendly viable product could be available to the society. He has informed that group is working on kW level battery stack and the project is funded by DST, MHRD, and IIT Delhi.

"The research team collected the operational data of the developed prototype in the field conditions, so that appropriate changes in the design and operation can be incorporated in the next scaled-up version," Prof. Verma added.

The facility was inaugurated by Prof. V. Ramgopal Rao, Director in the presence of Deputy Directors (Operations, and Strategy & Planning) and other dignitaries.

**What is VRFB:** VRFB utilizes liquid electrolyte to store electrical energy. During charging, the electrical energy is stored in the liquid electrolyte and during discharging the stored energy is used for various applications.

**How the VRFB based charging station works:** The flow battery charging station utilizes the VRFB, which is indigenously developed by the SERL team. The stored energy can be used to charge various portable electronic devices such as mobile phone, laptop, power bank, and tablet etc., using various charging ports provided in the flow battery charging station. The team has designed it for charging operation of around 9 hours in a day.

# KEY FEATURES OF VRFB



Inauguration of the portable flow battery based charging station by **Prof. V. Ramgopal Rao, Director, IIT Delhi**



The VRFB technology has the potential to efficiently store and utilize renewable energy for a wide range of applications such as rural electrification, e-vehicle charging station, commercial power back-up etc. leading to zero carbon footprint.

It is non-polluting (no emissions), easily scalable, safe and environment friendly, as well as highly durable. One of the major differences between the flow and conventional battery is the independent scaling of power and energy capacity.

The VRFB can store energy from kWh to MWh range and suitable for long discharge time with low cost in contrast to the conventional battery. The technology is highly suitable wherever diesel generators are used.

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# 2

## Greener and cheaper iron based redox flow batteries for energy storage applications

Project Reference No. DST/TMD/MES/2K16/83

In India the utilization rate of renewable energy is increasing and it is significant from the perspective of the nation's energy security and economic stability. Availability of renewable energy sources such as wind and solar are intermittent and unpredictable. Hence, storage of energy when generated becomes important. Several energy storage systems (ESS) have been developed. However, most of these storage systems have limited capacity, are expensive or use non-renewable and environmentally unfriendly materials and processes. To address this, suitable energy storage devices are crucial.

Scientists and engineers of "Energy lab" at "Center for Incubation, Innovation, Research and Consultancy" (CIIRC), Jyothy Institute of Technology Bengaluru has pulled off an arduous mile stone in the development of Iron electrolyte based Redox flow Battery (IRFB) funded by DST, under its flagship MES Scheme. The team has successfully tested lighting load of 1 kW using the developed flow battery and found that the battery has the capacity to power households across rural India thus having a societal and environmental impact besides being a potential competitor for various household and industrial batteries available in the market. The battery can be promoted as a cost effective and green system considering the materials used for development, electrolyte and the area of applications (Renewable energy sector), says the Principal Investigator Dr. H. B. Muralidhara along with his associates Anargya D, Ananth M S, Samarth B R, Archith Kamath, Dr. Santhosh M S, Dr. Geetha Priya and Dr. Narendra Kumar and coordinated by Dr. Ranjith Krishna Pai from DST.

The team has recently filed a patent on the same and part of their studies were published in leading international journals published by Elsevier and Springer.

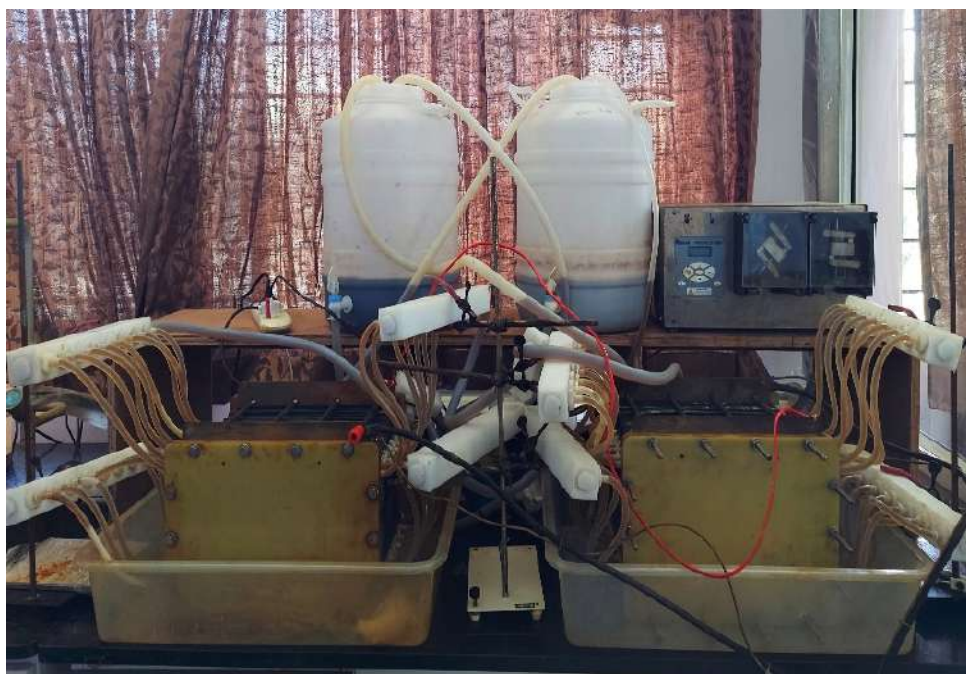



Fig. 1. The diagram showing the developed Iron flow battery with a load of 1 kW.



The Centre Head Dr. Krishna Venkatesh said 'The technology involves using a cheaper electrolyte developed at CIIRC being used. These electrolytes can operate at higher temperature than conventional vanadium electrolytes and are capable of storing 70% more energy. The batteries also offer a low cost of ownership than batteries that use other chemistries, such as lithium-ion batteries. He also shared on the fact that most of the components were developed indigenously and crucial parameters optimized.

Due to the flexibility, redox flow batteries usually have an excellent ability to be utilized as a means for energy storage. But however, batteries have suffered from two drawbacks that have inhibited their extensive use. The first drawback being the frequent use of environmentally dangerous and toxic heavy metal salts, like vanadium dissolved in sulfuric acid and used as electrolytes. The second drawback being the

evolution of hydrogen at cathode that hinders the life cycle of the battery due to varying pH of the electrolytes.

The team has added ligands to the iron electrolytes which will help avoid the pH imbalance of the electrolyte and increase the life cycle of the battery. Also for the first time different combinations of carbon/oxide based electrocatalysts have been experimented with to enhance the number of active sites on surface of graphite felt electrode used in IRFBs and introduction of additional functional groups were found effective to overcome the poor efficiency said Dr. H.B. Muralidhara the Principal Investigator of the project.

The team has future plan to propose a venture to develop and sell the Redox flow batteries to the Indian and global market and help achieve the last mile connectivity.

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# 3

## Exploring graphene-based nanocomposites for supercapacitor applications

Project Reference No. DST/TMD/MES/2K18/50

Owing to unique physicochemical properties, graphene-based materials are emerging in the field of energy storage devices, specifically, development of supercapacitors. One effective approach of improving the supercapacitor performance is to explore nanocomposite systems as active electrode materials. Herein, we have introduced conducting Polymer Polyaniline (PANI) over reduced graphene oxide (rGO) nanosheets to modulate the supercapacitor performance upon combining Electrical Double Layer Capacitance (EDLC) of rGO and pseudocapacitive behaviour of PANI, so called hybrid-supercapacitor. Here synthesized rGO-PANI nanocomposite exhibits vertically aligned nanowire arrays of PANI onto rGO sheets, resulting in an impressive supercapacitor performance. Boosting of Energy Density (ED) value upon usage of organic electrolyte is anticipated.

Extensive depletion of non-renewable energy sources fuels the demand for a renewable and efficient alternative of energy. Though energy can be harvested from renewable sources such as solar, wind, and hydrothermal, the geographical constraints bring unbalanced accessibility and thus efficient energy storage devices are sought after. A tremendous amount of research has been focused on the materials and technologies for energy storage, with batteries and supercapacitors being at the forefront.

1. In fact, batteries are currently employed for energy storage at various levels while the potential of the latter is yet to be unveiled to its maximum capacity.

2. Supercapacitors are foreseen as a better alternative for energy storage and are being explored heavily on the account of their high power density, remarkably long life cycle, and eco-friendly nature.

3. The bottleneck remains the low energy density due to which super-capacitors lag behind the other energy storing devices and various approaches have been followed to enhance the energy density without affecting the power density. Particularly carbon-based materials have been looked into

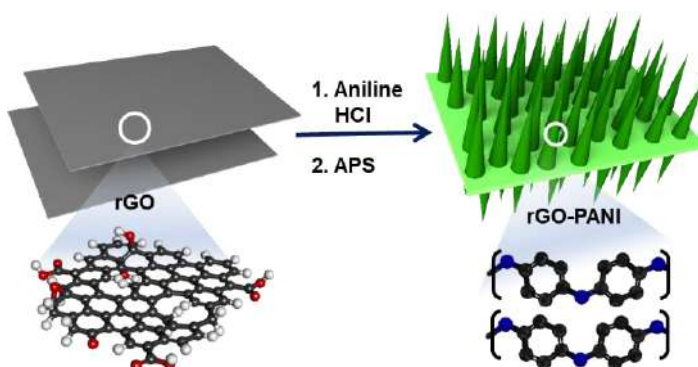
heavily as active material for supercapacitors. Graphene – a two-dimensional network of sp<sup>2</sup> hybridised carbons possess superior electrochemical performance but it is economically inefficient.

4. To overcome the high-production cost of graphene, chemically synthesized reduced graphene oxide (rGO) was explored which closely resembles pristine graphene and can be easily produced in gram-scale in laboratory following a top-down approach starting from graphite (Gr).

5. The supercapacitor performance can be enhanced when redox active materials such as metal oxides and conducting polymers are blended with rGO and introduced as active material, where the synergistic contribution of EDLC and pseudocapacitance can be realised.

6. The combination of rGO and PANI have been realised earlier as well where aniline to polyaniline conversion was carried out by different molar ratio of APS, ammonium persulphate (aniline:APS), however, the study of effect of varied concentrations of APS with respect to aniline on the nanocomposite was missing.

7,8. Herein, we have systematically varied the concentration of APS without perturbing the other reaction conditions (i.e., aniline concentration, temperature, acid concentration) and investigated the set of three nanocomposites; (1) rGO-PANI-1 (Aniline:HCl:APS = 1 : 1 : 0.6), (2) rGO-PANI-2 (Aniline:HCl:APS = 1 : 1 : 1), and (3) rGO-PANI-3 (Aniline:HCl:APS = 1 : 1 : 1.2). Out of all the nanocomposites, rGO-PANI-1 showed maximum electrical conductivity and hence it was tested



The polymerization of aniline over rGO matrix was carried out via oxidative polymerization process using APS in aqueous medium (Figure 1).

9. rGO employed here has been synthesized by following a reported protocol<sup>10</sup> to specifically get a mesoporous structure to enhance the electrochemically active surface area of the nanocomposites (Figure S1). Field-Emission Electron Microscopic (FESEM) images of rGO supported the porous structure and that of nanocomposites depicted the uniform formation of PANI over rGO sheets (Figure 2 and S2). Vertically aligned array of PANI nan-owires over rGO sheets is clearly visible in FESEM and High Resolution Transmission Electron Microscopic (HRTEM) images of all the three nanocomposites (Figure 2 and S2). It is noteworthy that such well-ordered PANI nanowires on rGO could be useful for the reduction of ionic diffusion path and enhancement of the percolation of ions in the interior parts, in turn maximizing the utilization of active electrode.

10. FTIR spectra of the nanocomposites were collected to probe rGO and formation of PANI in the nanocomposites. The bands at  $\sim 1728$ ,  $\sim 1621$ , and  $\sim 1064$   $\text{cm}^{-1}$  correspond to  $\text{-C=O}$ ,  $\text{-C=C-}$ ,  $\text{-C-O-C-}$  (epoxy) functional groups of rGO, respectively.<sup>11</sup> Also, the peak intensity reduced notably for rGO, compared to GO, indicating the successful reduction of GO to rGO (Figure S3a). Characteristic peaks for PANI at  $\sim 1560$  and  $\sim 1480$   $\text{cm}^{-1}$  for  $\text{C=C}$  stretching of the quinonoid and benzenoid rings, respectively along with the bands at  $\sim 1295$ ,  $\sim 1241$  and  $\sim 1125$   $\text{cm}^{-1}$  for  $\text{C-N}$  and  $\text{C-H}$  bending of benzenoid and quinoid rings confirmed the formation of PANI in the nanocomposites (Figure S3a).<sup>11-13</sup> The peaks corresponding to PANI are shifted to higher wavenumbers in the nano-composites which is attributed to the  $\pi$ - $\pi$  interaction and hydrogen bonding between rGO sheets and the polymer backbone.

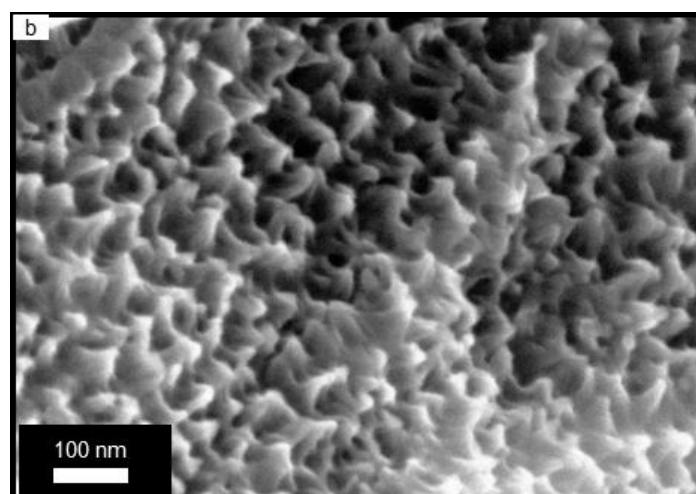
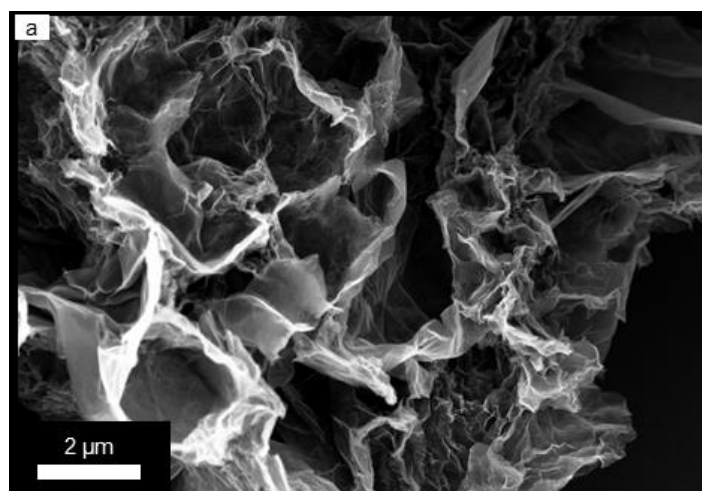


Figure 2. (a) FESEM images of (a) rGO, and (b) rGO-PANI-1.

12. To be around  $2.2 \Omega$  which is very small and the negligible charge transfer resistance (RCT) indicates the high power of the material (Figure S5c). The capacitance of rGO-PANI-1 nanocomposite was calculated from the CD plot and the value of capacitance was found to be around 450 F/g at a current density of 0.5 A/g which is very good. At a higher current density of 4 A/g the capacitance was more than 300 F/g which is noteworthy (Figure S5d). The maximum  $E_d$  and  $P_d$  of the material were calculated to be around 10 Wh/kg and 1000 W/kg, respectively (Figure 3b). Finally, we performed 1000 continuous charge-discharge cycles and more than 70% retention of capacitance and 100% re-tention in Coulombic efficiency were realized (Figure S5e). We strongly believe that using organic electrolyte will significantly boost the capacitance value likewise our rGO based supercapacitor.

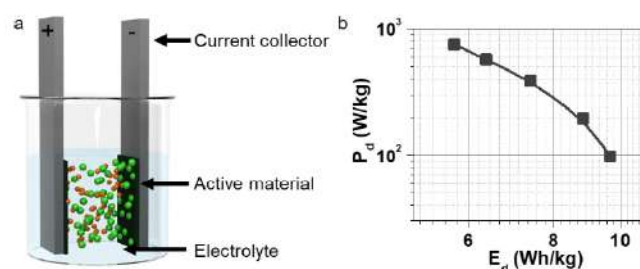


Figure 3. (a) Schematic of two-electrode setup for supercapacitor testing, and (b) Ragone plot of rGO-PANI-1.

14. In summary, we have successfully synthesized three rGO-PANI nanocomposites with varied aniline:APS ratio and rGO-PANI-1 with 1:0.6 ratio was observed to exhibit highest electrical conductivity. FESEM images revealed the vertically aligned array of PANI. Further, we have made electrode out of rGO-PANI-1 and tested its activity towards energy storage devices, specifically supercapacitor performance. The gravimetric capacitance value was found to be 450 F/g along with high

energy (10 Wh/kg) and power (1 kW/kg) density. This research will be useful in improvising the commercial prototype of rGO/Graphene-based Supercapacitors. Several prototypes as proof-of-concept have been developed at IISER Pune for product validation to be carried out at SPEL Pune.

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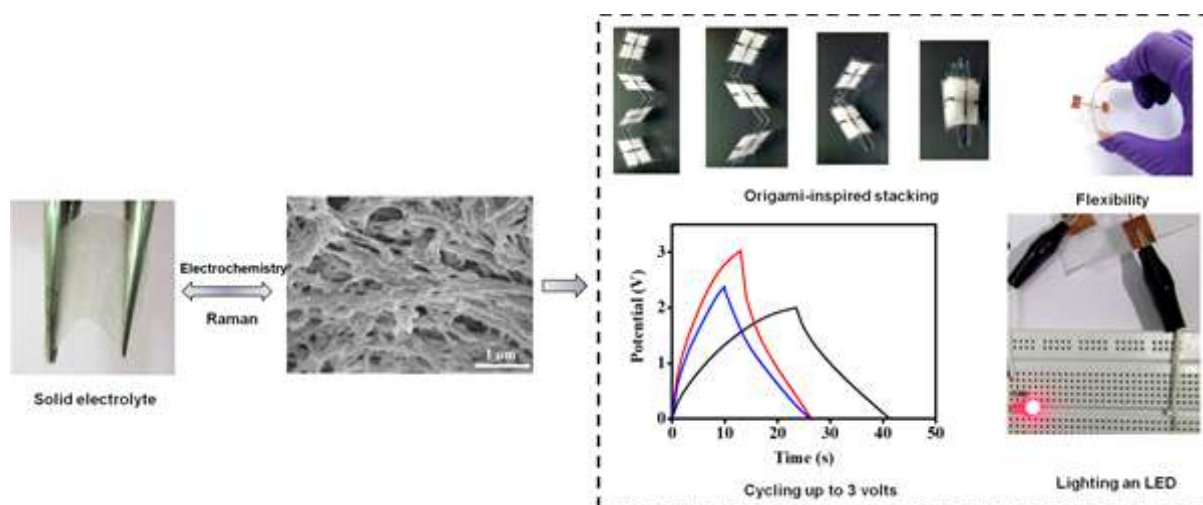
# 4

## Ionic liquid-based solid electrolyte for high performance wearable energy storage

Project Reference No. DST/TMD/MES/2K17/41


Flexibility in miniaturized energy storage components is one of the most sought-after and indispensable attributes in this smart era of Internet of Things. A major impediment that limits practical applicability is the low operational potential window of such flexible energy storage devices.

Conventional energy storage solutions employ ionic-liquid electrolytes for higher operational voltage. However, it is impractical to encapsulate ionic-liquid electrolytes for solid-state flexible devices. The challenge therefore lies in replicating the performance obtained with liquid-state ionic-liquid electrolyte in solid-state devices.



A frugal strategy developed by Prof. Subramaniam's group at the Department of Chemistry, Indian Institute of Technology Bombay overcomes this obstacle by suitably immobilizing ionic-liquid into a biopolymer matrix. Accordingly, a solid-state gel electrolyte with ionic-liquid as the active conductive component has been reported. Importantly, the investigation pin-points the design principle and method to optimise the ion-transport microstructure within the solid electrolyte and thereby achieve high performance from the supercapacitor. Further, the presence of such ion-transport channels has been directly visualized with the aid of micro-Raman spectroscopy. This enabled structure-property-function correlation for the solid-electrolyte and the final device.

A supercapacitive junction is fabricated by interweaving carbon nanotube wires across the solid-electrolyte, similar to how a tailor would sew up the clothes. This results in a supercapacitor being formed at every junction where two such threads intersect. "Such a simple yet elegant strategy to fabricate the device implies non-lithographic and scalable formation of microsupercapacitors" says Mihir Kumar Jha, the lead author of the study. Such a singular junction can operate up to 3 volts, which benchmarks its applicability for wearable electronics. The design and form-factor of the device also enables facile interconnection of multiple devices, by folding and stacking, similar to the Japanese art-form of Origami. In this way, a traditional Japanese art-form called 'origami' has been employed to enhance the overall performance of the device.



Since the device exhibits superlative performance metrics (50 Wh/kg; 4400 W/kg), the authors foresee immediate application of the device in the rapidly-evolving wearable industry. In fact, functional readiness of the device has been demonstrated by lighting-up a light-emitting-diode (LED) using a single junction.

This work is published in international peer-reviewed journals (ACS Appl. Electron. Mater. 2020, 2, 3, 659–669 and ACS Appl. Mater. Interfaces 2019, 11, 20, 18285–18294) and is funded and supported by the Technology Missions Division (Energy and Water) of Department of Science and Technology, India (DST/TMD/MES/2k17/41).

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## 5

# Covalent organic framework for light-weight charge storage devices

Project Reference No. DST/TMD/MES/2K17/103

Batteries and supercapacitors are probably the most practical energy-storage devices that can meet the global society's mobile energy demands. Mobility involves carrying weight; lowered weight means longer run duration before recharge. This reshapes gadgets of different sizes and needs, for example, from fit-bits to large automobiles. With batteries being the heart of every such device, if they can be made light-weight with high energy and power density, it would satisfy all needs. However, simultaneous high energy and power density is a challenge, and even bigger challenge is the rapid charging-discharging times and long cycle life. While capacitors help in rapid storage and release of charges (power device), batteries help in prolonged supply of power (energy device), but with a relatively slower expulsion of charges. The future mobile devices are going to be run by a hybrid supercapacitor-battery device. Intense research in this area involving new synthetic materials is not only academic but offers the opportunity of generating valuable IP and potentially a technology. With batteries being the heart of every such device, if they can be made light-weight with high energy and power density, it would satisfy all needs. However, simultaneous high energy and power density is a challenge, and even bigger challenge is the rapid charging-discharging times and long cycle life.

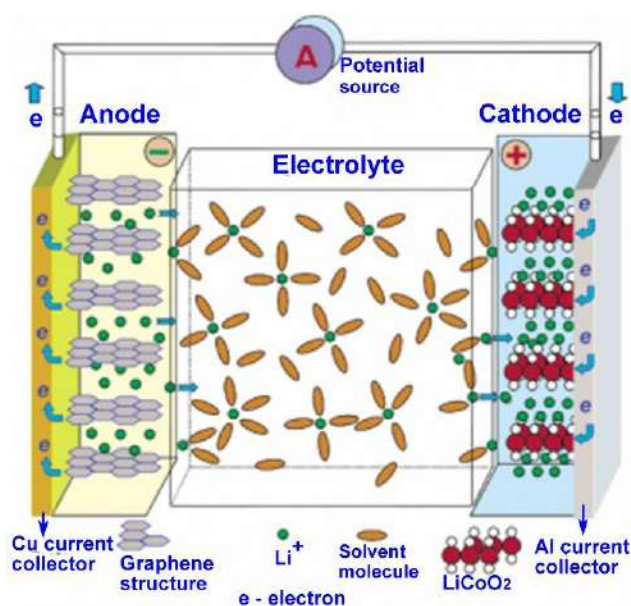


Figure 1. A Schematic representing the Li-Ion Battery. In this project we replace the graphite anode with COD.

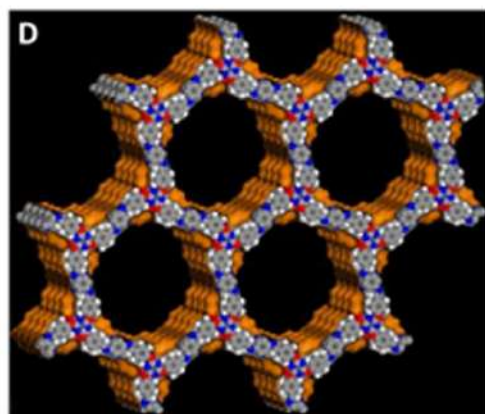
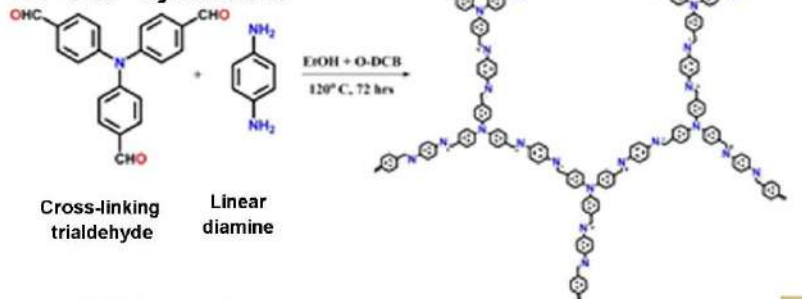
Currently, graphite forms the anode of a commercial metal-ion battery and inorganic oxides comprise the cathodes. Also, the graphite's theoretical capacity is already reached, which offers no further scope for enhancement of the anode performance. Meanwhile, the lithium supplying oxide-based cathodes are not easy to replace. Thus the anode offers room for improving battery performance. Making efficient graphite-like anodes with high energy and power density, rapid charging-discharging, and lightweight, but with more synthetic tunability is desirable.

Covalent Organic Frameworks (COFs) are crystalline organic polymers made of light atoms C, H, O, and N. These could be ideal candidates for a lightweight battery. COFs have many advantages (i) they can be made 100% crystalline with ordered nanopores. (ii) The structure can

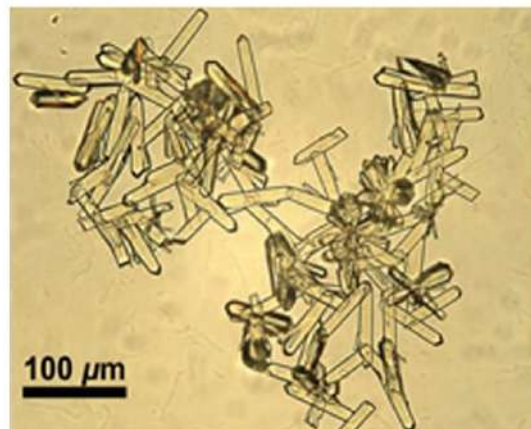
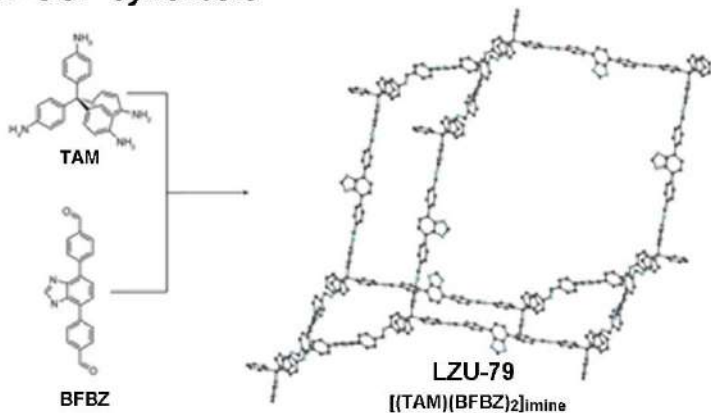
be determined to atomic-precision using crystallography and microscopy. (iii) Their framework composition and chemistry can be tuned at the molecular level. Now, if their organic framework is electronically tuned to be conducting/redox-active, they will probably be the best anodes with the lowest charge-transfer and mass-transfer resistances. At the same time, their conjugated framework can interact with the metal ions and provide a lot more active sites per gram and volume. Their large micro-mesopores can favor rapid-charge discharge characteristics.



### 2D-COF synthesis



### 3D-COF synthesis



**Figure 2.** An imine-linked 2D COF showing uniform mesoporous channels. These are typically obtained as polycrystalline powders. A 3D COF grown from tetrahedral building units. Pure homogeneous single crystals can be seen.

**Work at Advanced Porous Materials Lab, IISER Pune:** A COF framework can be enriched with heteroatoms (N, P, S) to make it more interactive with Li-ions, and can be made to store much more Li-ions than what graphite can store.

One of our projects aims at exfoliating such N-rich COF to few-layer thick nanosheets capable of allowing for rapid diffusion of Li-ions. The exfoliation of the COF themselves can be brought about by a mechanical method such as sonication or a more controlled chemical method. We have designed a concept of "Functional Exfoliation Agent" (FEA) a chemical exfoliation, where the chemical species covalently bind to the COF layers and strips them apart (without disturbing the in-plane layers). Notably, the FEA themselves carry pre-designed metal-ion interaction sites. Thus, the chemical exfoliation carried out using FEA will result in functionalized COF nanosheets, with increased metal-ion interaction sites and enhanced mass and charge transfer characteristics. Such COFs can be engineered to anodes for Li-ion batteries with superior gravimetric capacities, making them tailored for mobile batteries. Their organic nature enables them to blend well with several bulk materials such as polymers, papers, textiles and inorganics. This brings advantage when it comes to making battery electrodes.

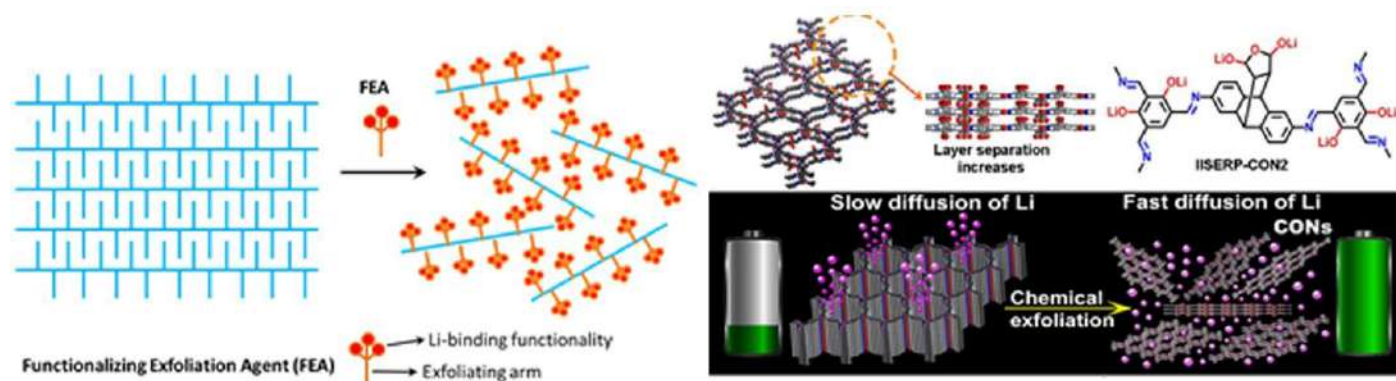


Figure 4. Left: A schematic illustration of the "Functionalizing Exfoliation Agent (FEA)" concept in COF. Right: A Diels-Alder chemical exfoliation of COF and it shows how the exfoliation can increase Li-ion loading and speed of loading.

In another aspect, we make COF-anodes that have pre-designed electron-rich and deficient modules, and their stoichiometry can be adjusted to favor an overall electron-deficient framework. When made as anodes, such frameworks will show a natural tendency to accept and accumulate electrons flowing in from the external circuit. This electron-richness at the anode, in turn, will set-up a driving force for the positively charged metal ions from the electrolyte. The rapidity of the metal-ions flow will directly impact the charging and discharging rates.

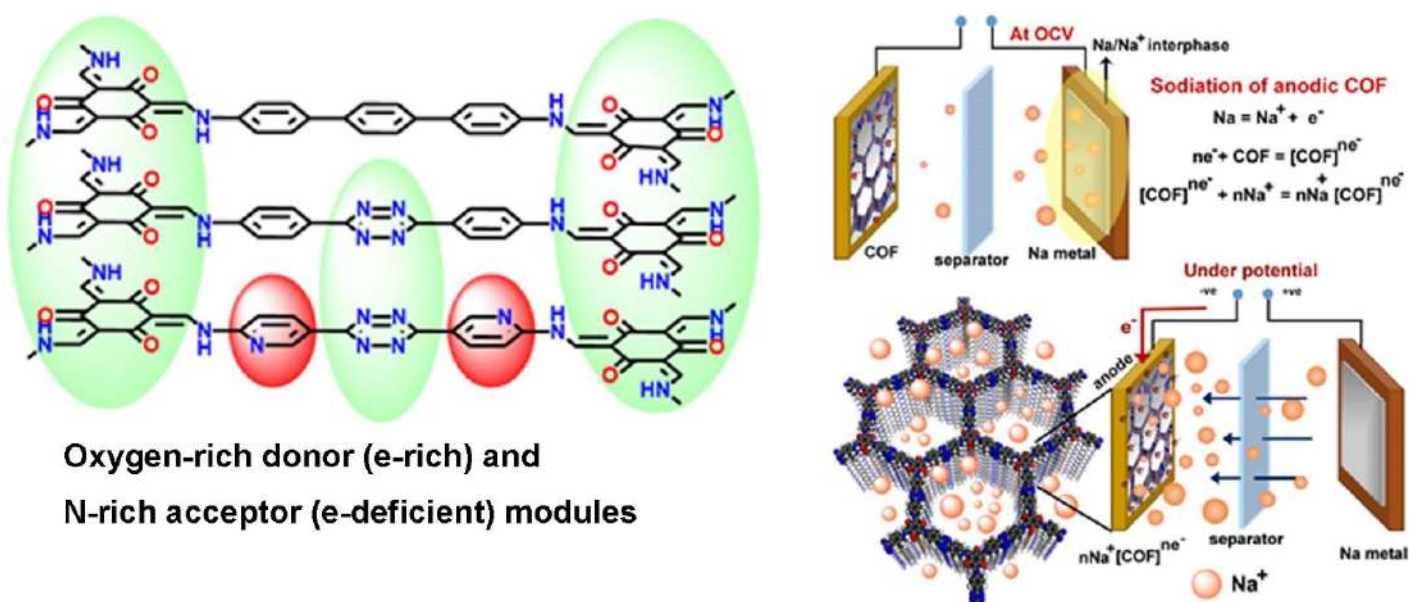


Figure 5. Left: Left: A Zoom-in on the electron-rich and deficient modules of the COF, The higher concentration of N-rich, e-deficient centers makes the COF e-deficient. Right: The battery anode made of such COF sucks electrons from external circuit dirfing force for the incoming Na+ ions.

Such a design would be extremely advantageous for making lightweight rapid charge-discharge sodium-ion batteries. Due to their relatively large size and unfavorable thermodynamics when it comes to interacting with carbon anodes, Sodium ions have not qualified for practical battery applications. As explained above, we will make specialized anodes for sodium-ion batteries by tuning the electronics of the mesoporous COFs. Given the abundance and low cost of sodium compared to lithium, this would allow a game-changing battery technology.

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# 6

## The sodium way of charging devices

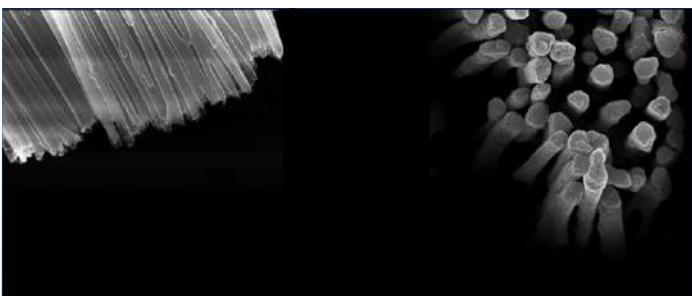
Sodium-based hybrid energy storage devices: from wearable to miniature applications

Project Reference No. DST/TMD/MES/2K16/114

Everyone wants energy storage devices that gratify their needs. For instance, someone who struggles with a tangle of charger wires on their office desk would dream of batteries with capacity that could last for weeks. Electric vehicles have to be competitive with gasoline-driven cars. Otherwise, electric car drivers might want to carefully plan their routes to avoid being stranded far from a charging station. Miniaturization for the Internet of Things (IoT) designs will require better-performing micro-supercapacitors. In the future, we might also want to power tiny wearable, flexible electronics with miniature storage devices. Therefore, it is crucial to understand that there is no one “Energy Storage Device” that can satisfy all our needs. From humongous Tesla's power pack that can deliver 730 MWh of energy at Monterey, Australia, to tiny batteries that power more than 600,000 pacemakers each year worldwide, the applications are poles apart.

At the Indian Institute of Science Education and Research Thiruvananthapuram, a team led by Dr. M.M. Shaijumon, Associate Professor, explored various materials for such application-specific hybrid energy storage devices. With financial support from the Department of Science and Technology (DST/TMD/MES/2K16/114), the group undertook an in-depth investigation of the performance of nanoarchitected electrodes for microscale Na-ion battery and Hybrid-Ion Capacitor (HIC) devices. An application-specific route was also envisaged to develop microelectrodes for micro-batteries and flexible Na-ion capacitor devices with engineered electrodes and electrolyte/separator.

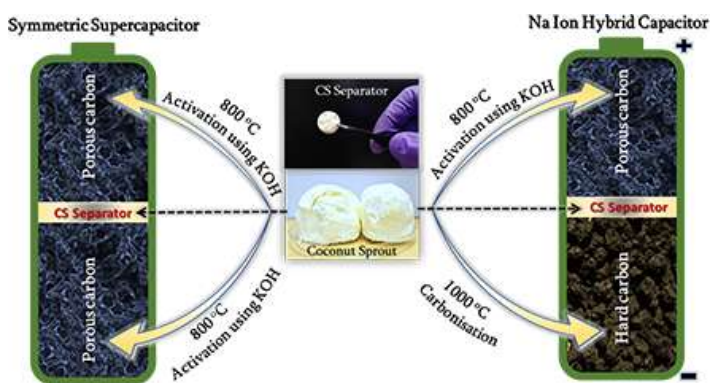
Owing to the growing concerns over lithium resources worldwide and the on-going thrust on sodium chemistry due to their vast abundance and similar electrochemical property with that of lithium, a drift towards sodium-based ion batteries is quite prominent in the research community. When it comes to device performance in terms of energy and power densities, ion-batteries and supercapacitors, the two most widely used storage devices, stand face off. Batteries offer better energy density, whereas good power density is achieved with the latter. Instead of separating a battery and a supercapacitor from one other, why not integrate both battery and supercapacitor into one energy-storing device instead of separating one from the other? The offspring would be a “Hybrid-Ion Capacitor” (HIC), a novel design structure that could enhance the symbiotic benefits of rechargeable batteries and supercapacitors.



Though the recipe for the synthesis of anode materials for sodium is much the same as for lithium-based devices, the chemistry is quite unlike. The team at IISERTVM has been able to successfully synthesize anode materials such as brown titania,  $\text{Na}_2\text{Ti}_9\text{O}_{19}$ ,  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  for hybrid ion capacitors. Further scaling-up of existing NIC devices developed from this DST project, and the development of 18650 hybrid ion capacitor devices would be the direction in which the team is focused.

In this venture, the group has meticulously published more than ten research articles in various SCI journals. Studies on kinetics and diffusion characteristics of lithium ions in  $\text{TiNb}_2\text{O}_7$  carried out by Dr. Binson Babu, formerly a doctoral student at the group were recently published in *Electrochimica Acta*. The work encompasses techniques like using galvanostatic intermittent titration technique, electrochemical impedance spectroscopy, and cyclic voltammetry.

In search of sustainable strategies for the preparation of electrode materials for energy storage device following strict environmental requirements, for the first time, use of coconut sprout (CS) as a single precursor to prepare highly efficient carbon-based anode and cathode materials and a separator with excellent mechanical properties and good chemical stability towards the fabrication of a hybrid sodium ion capacitor device was explored as a part of the project.



Flexible hybrid-ion capacitors find potential applications in flexible electronics to meet the energy requirements of wearable gadgets. New versions of pacemakers, medical patches, and drug delivery systems use flexible and thin power sources in the medical field. The size and flexibility of flexible batteries entirely comply with these requirements. Thus, the

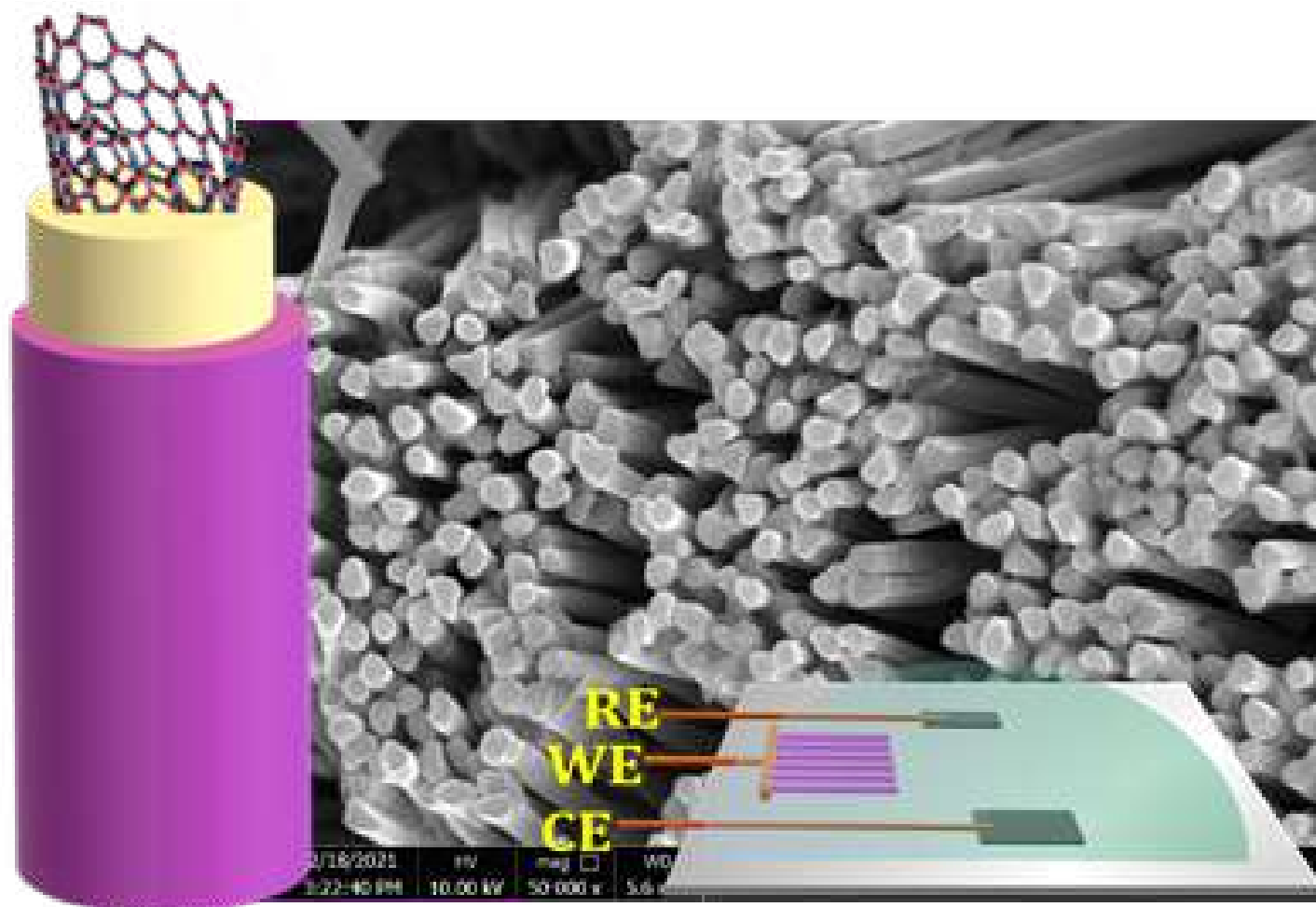
medical devices segment holds a significant share of the flexible battery market. One among the outcomes of the project is the initial efforts undertaken to fabricate graphene-based flexible electrodes. A pouch cell working device made with a flexible graphene-based electrode and PVdF HFP gel electrolyte and its proof-of-concept demonstration by lighting a bunch of LEDs in a moldable state.



### Flexible hybrid-ion capacitor

Dr. Shaijumon's interest in developing miniature energy harvesting and storage devices dates back to his postdoctoral days at Prof. Pulickel M Ajayan's Lab at Rice University. The group presently explores the possibility of developing a coaxial micro-HIC. "Just as any conventional electrochemical HIC, the electrons must flow through a circuit connecting two coaxial electrodes separated by a polymeric electrolyte. A preliminary experiment to grow  $\text{C}_w$ ,  $\text{MoS}_2$ , CNT, and Ni-based nanorods as interdigitated finger electrodes with vertically aligned nanorods are being carried out. Upon optimizing the growth parameters, growth of polymer wrapped electrodes will be carried out, and their electrochemical properties will be investigated", says the Principal Investigator.

The Nanomaterials and Energy Devices Group @ IISERTVM, led by Dr. M.M. Shaijumon, continues their intensive efforts to focus on hybrid nanostructures, organic electrodes for Li/Na/K ion batteries, miniaturized energy storage devices, and hybrid ion capacitors towards combining energy & power. Just as the lithium-ion batteries made a revolution by changing the way people communicate, the journey of battery research has bundles of exciting avenues yet to be explored for a greener environment and benefit of humankind.



**Ni-based nanorods**

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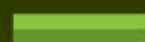
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**SOLAR**



**WIND**



**WATER**



**TREE**



**INDUSTRY**





# 7

## PCM integrated solar powered space heating system

Project Reference No. DST/TMD/MES/2K16/95

Northern India receives considerable solar energy, while at the same time has a large demand for space heating. Solar space heating, combined with a thermal energy storage using PCM could play a very important role in maintaining comfort conditions i.e. 15-20°C in the cold regions where the temperature goes down to -15 to -20°C. This paper presents experimental results for using various PCMs i.e. HS22, HS29 and HS34 used for maintaining the comfort conditions, tested in small-scale setup and real scale setup. The results show stabilization of the temperature of the test room, PCM type and required PCM quantity.

India's total installed electric capacity is 356 GW . India's energy consumption has almost doubled since 2000 and the potential for further rapid growth is enormous. Yet the increase in domestic energy production is far below than India's consumption needs. By 2040 more than 40% of primary energy supply will be imported, up from 32% in 2013. Consequently, there is a large latent demand for energy services that needs to be fulfilled in order for people to have reasonable incomes and a decent quality of life . It is estimated that 30% of the capacity in moderate climate and 70% in cold areas is for space heating . Not only in India, 40-50% of US homes depend on electricity based heating systems and 69% of Europe's total electricity consumption is because of space heating . About 5000 trillion kWh/year of energy is incident over India's land area. Northern India receives solar insolation of 3-7 kWh/m<sup>2</sup>/day . Solar energy plays an important role in responding to the growing demand of energy as well as dealing with pressing climate change and air pollution issues. Solar energy is featured with low-density and intermittency, therefore an appropriate storage method is required . Thermal Energy Storage (TES) has become very important in the recent years since it balances the energy demand and can improve the efficiency of solar systems. It is important that the TES have the necessary characteristics to improve the performance of the solar-based systems. The conventional TES in building applications is water, that is used in the heating system. Recently, PCM technology improvement helps to use different types of PCMs for increasing energy and exergy efficiency of TES system . Usage of PCM for TES provides a great benefit but their low thermal conductivity can be a major drawback. This can be compensated with the use of phase change material in an appropriate design for effective functioning of the system . The most sensitive parameters affecting the performance of a TES with PCM are the melting point of the PCM, mass of PCM, and airflow rate .

Unlike conventional sensible TES materials, PCMs allow much higher energy storage densities in a small temperature range and the heat is stored and released at an almost constant temperature. PCMs can be used for both active and passive space heating and cooling systems . In passive systems, PCMs can be encapsulated in building materials such as concrete, gypsum wallboard, in the ceiling or floor to increase their thermal storage capacity. They can either capture solar energy directly or thermal energy through natural convection. Increasing the thermal storage capacity of a building can increase human comfort by decreasing the magnitude of internal air temperature swings so that the indoor air temperature is closer to that desired over a longer period of time. Alternatively, a TES unit using PCMs can be used with conventional active space heating and cooling systems to improve the overall thermal efficiency as well as to reduce the peak heating and cooling electrical load. PCMs can also be incorporated in conventional heating or cooling systems so that its capacity can be reduced. Considerable research has been done on the application of PCMs for

space heating and cooling, yet at present there are few systems in use. Latent heat thermal energy storage (LHTES) is becoming more and more attractive for space heating and cooling of buildings. The advantage of using space heating of buildings is the ability to store the heat during the day and using it later in the night continuously, particularly in the winter by reducing diurnal temperature fluctuations.

The Solar Heating & Cooling program of International Energy Agency (IEA) states that space heating and cooling demand account for over 75% of the energy consumed in single and multi-family homes. In contrast to conventional methods for thermal storage using water, phase change materials (PCMs) provide heat storage at nearly constant temperature and possibly much higher heat storage densities. This technology can meet up to maximum of the demand depending on the region's climate. Active and passive systems are used for this purpose.

In this paper, the experimental results of solar space heating system with a TES using PCM are presented, from testing a small scale and a real scale setup. Both setups contain a TES using PCM, situated in a test room that is the space to be heated, and surround by a cold room that assures the cold ambient conditions of the test room, as in a cold night. The small-scale setup serves to experimentally test first parameters of the design, on a small scale and in a simplified situation. Following, based on the results of the small-scale setup, tests were performed in a real-scale setup, which is not only on a real-scale but also includes air ducts with fans and solar collector being exposed to the sun. The test location, determining the solar irradiation, was south of Delhi.

## Experimental set ups and respective goals of testing

The small-scale setup was designed and tested for proving the concept; the main objective was to study discharging cycle of the PCM. PCM modules with the PCM already in the liquid state were therefore introduced into the TES. The test room with the TES inside, was placed in the cold room to assure an ambient temperature of  $-20^{\circ}\text{C}$  for the test room as shown in Figure 1.

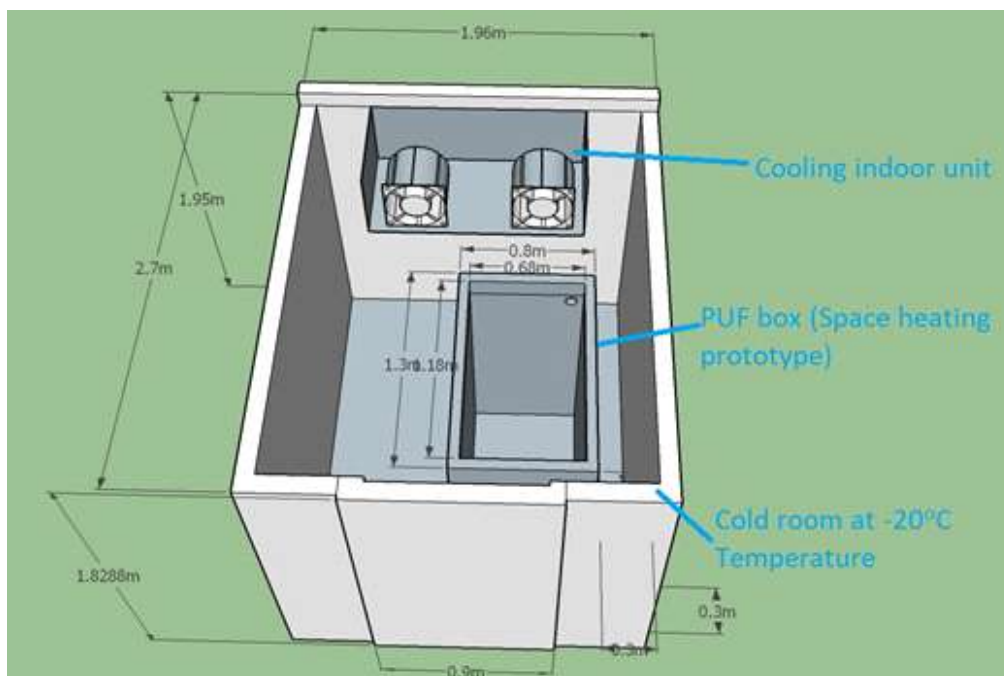


Figure : Sketch of the whole small-scale setup, including test room, the cold room, and their dimensions

The TES in the small-scale setup was tested with three different PCMs; HS22, HS29 and HS34 .

The small-scale setup serves to experimentally test first parameters of the design, on a small-scale and in a simplified situation. Following, based on the results of the small-scale setup, tests were performed in a real-scale setup, which is not only on a real-scale but also includes air ducts with fans and solar collector being exposed to the sun. The test location, determining the solar irradiation and the sunshine and non-sunshine hours, was south of Delhi.

The real-scale setup is shown in Figure 2 . Figure 2 shows a sketch of the whole real-scale setup, including test room, the cold room that assures the cold ambient temperatures of the test room, the TES in the test room, and the solar collector with ducts that connects both, in 3-D. The cold room, which can be programmed to simulate any ambient conditions. For the current studies and experiments, the cold room was consistently maintained at -20oC. The solar collector was an evacuated tube collector (ETC).

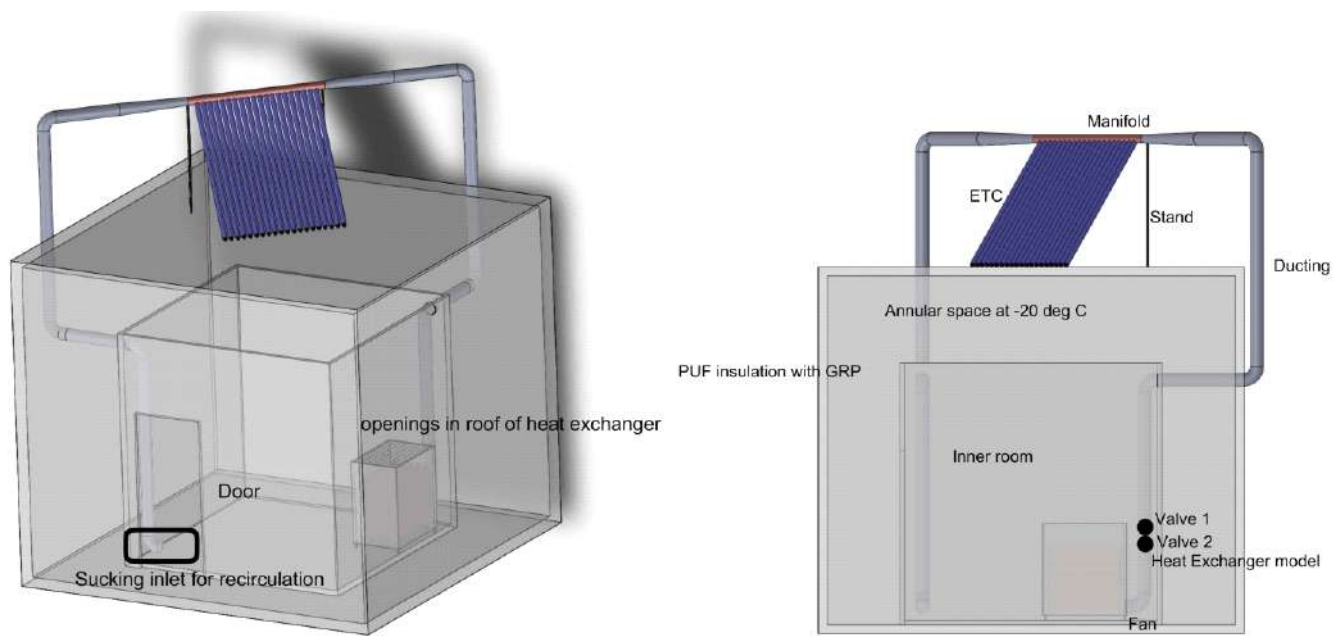


Figure 2 : Sketch of the whole real-scale setup, including test room, the cold room, TES, solar collector with ducts, in 3D

S.No	Particulars	Specifications
1	TES (MM)	840x200x20
2	HDPE Extrude Panel (MM)	1180x1380x680
3	TES Insulation Thickness (MM)	25
4	Power of the Fan (W)	62
5	Fan Type	Inline Duct Fan
6	PCM	E® HS29
7	Total PCM Quantity (KG)	110

# Experimental procedure and results

## Small-scale setup

The small-scale setup was designed and tested for proving the concept, and serves to experimentally test first parameters of the design, mainly the type of PCM and the amount, on a small scale and in a simplified situation. The main objective is to study the discharging of the PCM. PCM modules with the PCM already in the liquid state were therefore introduced into the TES, and the temperature profile inside the TES and center of the test room was monitored.

In small scale setup, PCM encapsulations, high-density polyethylene (HDPE), were filled with three different type of PCMs, HS22, HS29 and HS34. PCM was charged manually in an ambient of 50°C. Temperatures at different points as shown in Figure 2, was recorded. Time vs temperature plot is shown in Figure 3.

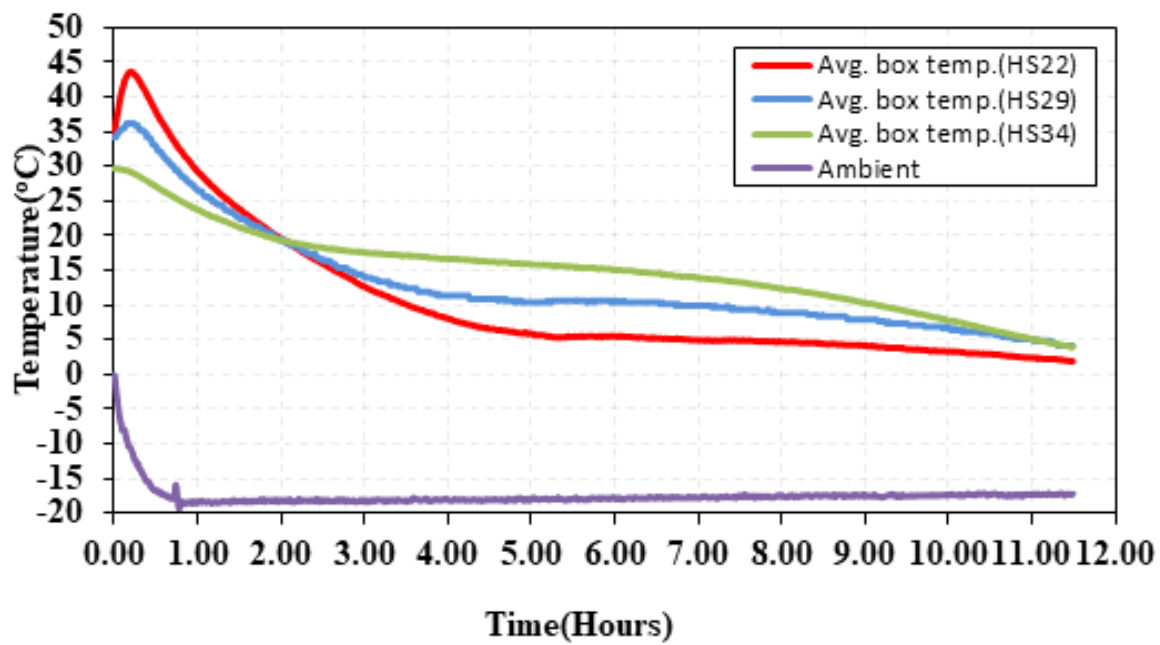


Figure : Average temperature variation inside the small scale setup for different PCMs

# Real Scale Setup

In real scale setup, both charging and discharging cycle were studied. Evacuated tube collector (ETC) was set up facing south. Radiations collected by the tubes transfer heat to the heat pipe, which in turn allows fluid to boil and rise within the tube. The tip of the heat pipe ends in a duct through which air is allowed to pass. Flow of air is controlled by duct fan connected with the heat exchanger through suction. Heat pipe transfers heat to the flowing air via fins installed within the duct. Duct fan pulls the air from the duct and pushes it into the heat exchanger. Heat exchange with the PCM panels takes place which melts/ charges the PCM. During non-sunshine hours, a valve closes the passage of air coming from the solar air collector and allows air circulation within the room (space heating). Because of cold climate conditions in the cold chamber (ambient), heat flows from heat exchanger to the room, thereby controlling the temperature in the desired range.

Early morning, collector inlet temperature was at 15oC and the collector outlet temperature at 30oC. During peak sunshine hours, collector outlet temperature increased to 50oC. Temperature in the cold chamber (ambient) is maintained between 0 to -5oC during sunshine hours and -10 to -15oC during off sunshine hours.

Peak 1 at collector outlet temperature was observed when valve was closed in the evening around 5.30pm. Diffused radiation collected by the ETC during this period builds up temperature in the collector. Similarly, Peak 2 was also observed in the morning when diffuse radiation in morning are captured by ETC before opening the valve for the second cycle.

Temperature in the room (space heating) was recorded as 15oC when PCM was in completely discharged condition. Temperature variation during the entire day varies between 10oC to 25oC. Maximum temperature in the room (space heating) was recorded as 25oC at around 05:00pm and then it starts decreasing as soon as the valve is closed during off-sunshine hours. The room (space heating) temperature was recorded 15oC till 5:00am in the morning and after that maintains between 10-15oC temperatures for next 3-4 hours. Backup hours of approximately 11 hours was achieved during off sunshine hours.

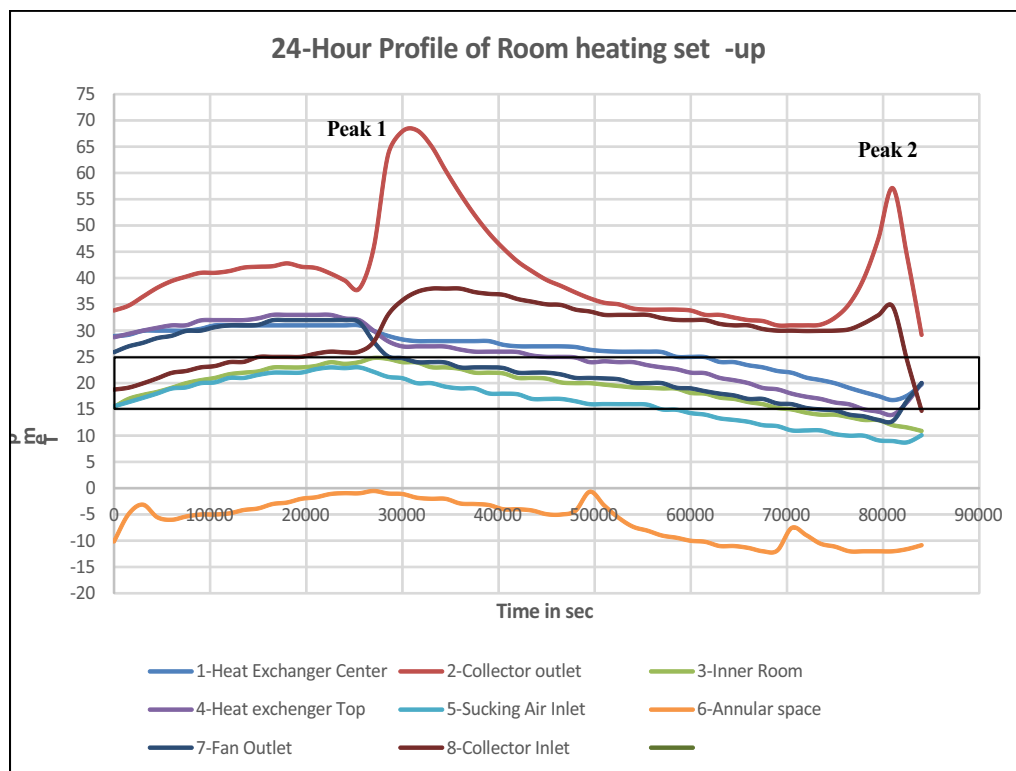


Figure 4 : Temperature variations in inner room and at other locations

The results from real scale setup indicates that the PCM save<sup>E</sup> HS29 is suitable for maintaining the room (space heating) temperature in the range of 15-25o C. 34oC PCM can maintain room (space heating) temperatures in higher range but charging during sunshine hours might be challenging in some areas. The systems based on renewable energy aims to curb the GHG emissions and provide means of thermal comfort without burning fossil fuels. The results obtained so far are encouraging enough to plan for the system, which can aim to bring down CO2 emissions substantially. We aim to design a setup, which can provide heating solutions where electricity is not available. High altitude areas are abundant with sunshine and extreme cold conditions make human survival a difficult task. The two factors are encouraging enough to follow the path.

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# 8

## Inkjet printing of energy storage materials on paper/ textile substrates and their application for flexible supercapacitors

Project Reference No. DST/TMD/MES/2K17/05


The flexible electronics have recently emerged as a game-changer technique, which has created enormous possibilities to improve the existing electronic systems. The next generation of smart electronic devices needs high-performance power sources that can be easily integrated with shape and size versatile electronic components. Here, we demonstrate inkjet printing method for easy manufacturing of thin-film supercapacitors on all printable substrates including paper and cloths. The energy storage materials were converted to the printable inks by optimizing their physical properties. The printed supercapacitors with different shapes, sizes, and thicknesses were fabricated using a commonly used desktop printer. These supercapacitors demonstrate excellent electrochemical performance including high power density, high energy density, long lifetime, high rate capability, and low series resistance. These devices also exhibit excellent flexibility, repeatability, and reproducibility. Therefore, inkjet printing has a huge potential for development of flexible energy storage devices for flexible and wearable electronics area. Although development of flexible energy storage devices is at the fledging stage and further research attention is required to use them for real-life applications.

The rapidly increasing demand for flexible/ wearable electronic devices and internet of things (IoT) have captured worldwide attention towards the easy manufacturing of light-weight, portable, low-cost, highly flexible, and high-performance energy storage devices. [1-3] The applications of these smart devices range from the electronics used in our daily lives (smartphones, wearable devices, laptop, etc.) to the medical (wearable healthcare devices and medical implants) and industrial applications (electric vehicles, nano-robots, micro-electromechanical systems, wireless sensors, etc.).[4] The upcoming flexible devices require highly flexible and

miniaturized power sources, which may easily and precisely integrate with them to fulfill their power requirements. Traditional energy storage systems, including batteries and supercapacitors (SCs), possess several disadvantages such as; rigidity, heavyweight, and large overall volume, which fail to meet the versatile form factor and flexibility requirements of the flexible electronic systems. [5-9] Recently, some flexible batteries and SCs have been reported with bendable and foldable features, which have provided a foundation for further work in this area. The performance of the developed devices is still inadequate from a practical standpoint due to the excessive use of

aqueous electrolytes, the overall high cost, complex processing methods, and improper design of device components. Out of the different energy storage devices such as batteries, supercapacitors, and the electrolytic capacitors, the micro-supercapacitors have displayed the huge potential for the miniaturized electronics applications, due to their high rate capability, long lifetime, and easy integration.[10] The performance and the scalability of the micro-supercapacitors also depend on the selection of the fabrication method. The widely used fabrication techniques are printing, lithography, laser scribing, chemical vapor deposition, and





electrochemical/ electrophoretic deposition. [4, 5, 11-14] The most of the methods have several problems like; complex procedures, poor scalability, time-consuming nature, expensive, and high waste residue. Among the different techniques developed in this area the inkjet printing is one of the smart technologies that eliminate some key scalability problems.[15] It uses direct deposition of digitally pre-designed patterns that provide full control over the localization, shape, size, thickness, and architecture of the printed electrodes on different substrate surfaces.[16] The unique features of this method are its simplicity, low-cost, non-contact deposition, no material wastage, and environmental friendliness. In recent years, the application of the commercially available desktop printers for development of SCs and batteries has significantly reduced the cost of the printed energy storage devices, and subsequently, their production process has also been greatly simplified.[4, 11] Despite the several advantages that they may possess, the major limitations of this method for its broad application are the development of the printable ink with rigid physical properties which will not clog the printing nozzle and print continuously. [17-19] According to the literature[17], the printable ink for the drop-on-demand printer should have a specific range of the viscosity, surface tension, and density and the Fromm number (Z) must be in the range of  $4 < Z < 14$ . [18] The selection of suitable electrode material is one of the critical

factors of energy storage devices, which directly affects their performance. Therefore, significant efforts have been devoted to their improvement.[20] The several materials have been widely used as excellent energy storage materials, including transition metal oxides/ sulfides,[21, 22] conducting polymers,[23, 24] carbon-based materials,[4, 25] and their composites;[11, 26]. However, their processing for printable inks and their use for flexible energy storage devices is not well developed.

In consideration of the existing problems for fabricating flexible supercapacitors, we report an inkjet-printed, solid-state, and highly flexible supercapacitors on low-cost and commonly used substrates such as paper and textile. The presented approach can be further extended to develop other high performance printed electronic devices, which may be promising for the next generation of the energy storage devices and flexible electronics applications.

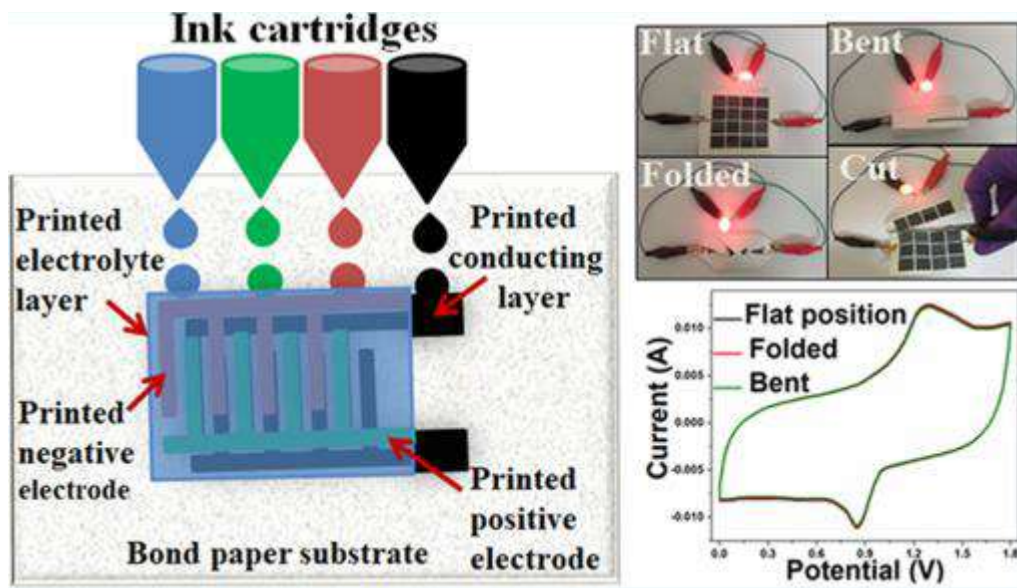


Figure 4 : Schematic of the printed micro-supercapacitors, demonstration of the printed micro supercapacitor for real-life applications (3.2 V LED), device performance in the flexible condition.

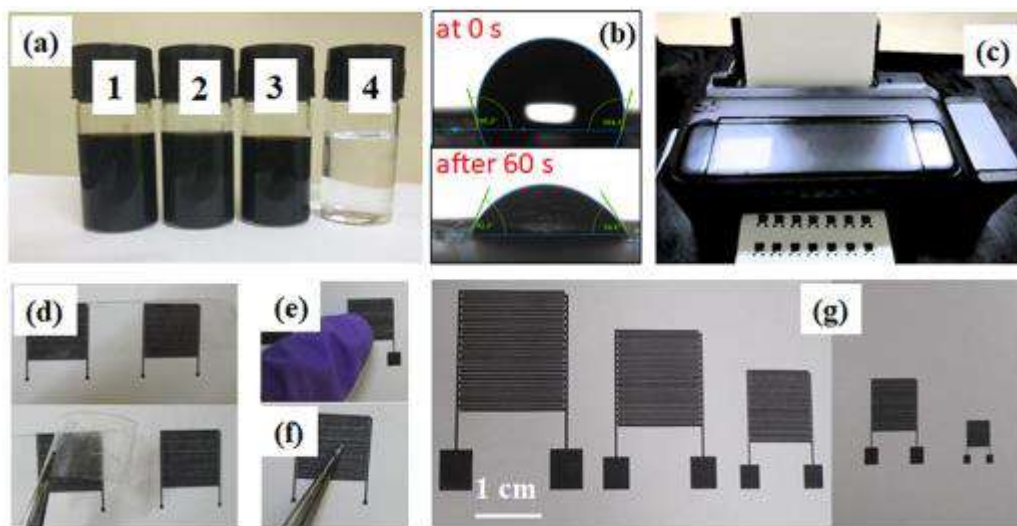


Figure 4 : (a) Photographs of the different inks (1, 2, 3, and 4 symbolize conducting, the negative electrode, positive electrode, and electrolyte inks, respectively). (b) Variation in the contact angle of the ink on bond paper substrate with time. (c) Printed SCs using a desktop printer. (d) Tape test and (e, f) mechanical rubbing test of the printed SCs. (g) Photograph of the printed SCs with different sizes.

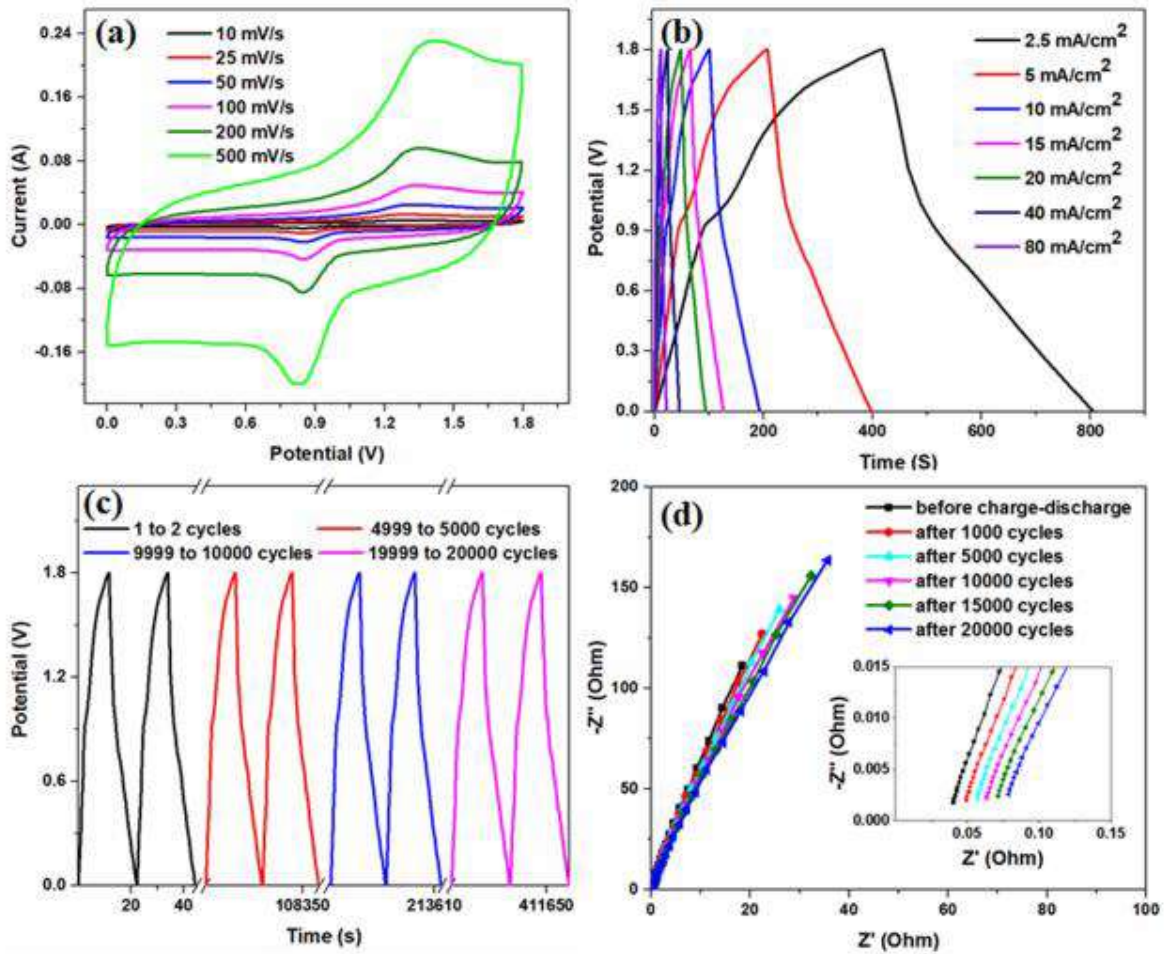


Figure 3 : Electrochemical performance of an optimized AC-Bi<sub>2</sub>O<sub>3</sub>//rGO-MnO<sub>2</sub> P $\mu$ SC device: (a) CV curves at different scan rates, (b) GCD curves at various current densities in the voltage range of 0 to 1.8 V, (c) GCD curves at a current density of 80 mA/cm<sup>2</sup> up to 20 000 charge-discharge cycles, and (d) Nyquist plots in the frequency range of 0.01 Hz to 100 kHz at different cycle life instants (inset is the magnified plot of the high-frequency region)

Figure 3 demonstrates the excellent electrochemical performance of the printed supercapacitors. The as-prepared devices displayed admirable electrochemical performance, including high energy and power density (energy density of 13.28 mWh/ cm<sup>3</sup> at a power density of 4.5 W/cm<sup>3</sup>), excellent rate capability (80% retention of capacitance as the current density increases by 32 times), excellent frequency response (a time constant of 0.09 ms), and high cycle stability (92.2% retention of capacitance after 20 000 cycles). In addition, the presented method is highly scalable, with control over the device thickness, dimensions, size, shape, and implementation through one printing step defined through the computer-aided design layout. The devices also show outstanding flexibility, reproducibility, and repeatability (as indicated by excellent capacitance retention in Figure 4).

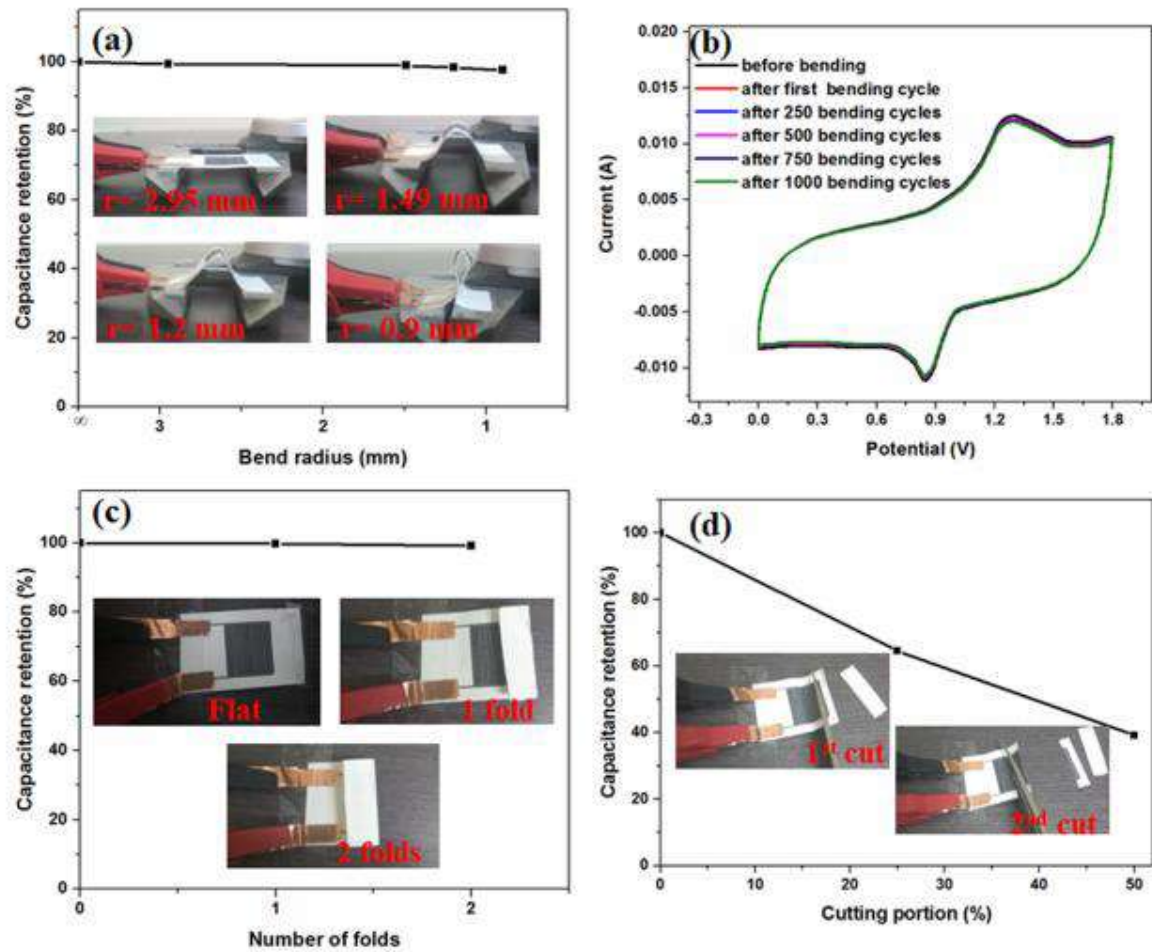


Figure 4. Electrochemical performance of the P $\mu$ SC device under different conditions: (a) capacitance retention at different bending radii, (b) variation in CV profiles of the device after different bending cycles at a bend radius of 0.9 mm, (c) capacitance retention at different folds, and (d) capacitance retention in cutting condition. Inset images are the digital photographs of the device at different conditions.

The other development is the printed, binder-free, flexible, and high-performance NiCo<sub>2</sub>O<sub>4</sub>// Reduced Graphene Oxide (rGO) battery-supercapacitor hybrid device on cotton fabric substrates. The NiCo<sub>2</sub>O<sub>4</sub> micro-flower arrays were successfully fabricated over the cloth substrates using printing and low-temperature heat treatment method. The crystalline and conducting NiCo<sub>2</sub>O<sub>4</sub> micro-flower array layer acts as a self-supporting electrode, and its open space structure ensures the fast electron transport and full utilization of the electrode surface. The printed NiCo<sub>2</sub>O<sub>4</sub> // rGO asymmetric device with the LiCl –PVA gel electrolyte displays good electrochemical performance within a potential window of 0 to 1.6V. The fabricated device exhibited excellent electrochemical performance including high areal capacitance of 7.2 F/cm<sup>2</sup> (2650 F/g) at a current density of 1 mA/cm<sup>2</sup>, good cycle life (89 % capacitance retention after 5000 charge-discharge cycles), high rate capability, high power density, high energy density, and low charge transfer resistance both in the normal and flexed conditions. The obtained results are comparable to the existing literature for the high temperature processed NiCo<sub>2</sub>O<sub>4</sub> based energy storage devices, and therefore the reported method has a great potential for the direct fabrication of electrode materials over the temperature-sensitive fabric substrates. These fabric-based supercapacitors can be easily integrated with various flexible and wearable devices and exhibit a great benefit for the next generation of wearable electronic devices. We are further working on the proper packaging of the inkjet-printed flexible supercapacitors, integration of the devices with wearable electronics.

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# 9

## Scaled-up synthesis of high power Li-ion battery materials-indigenous technology development

Project Reference No. DST/TMD/MES/2K17/11

High power Li-ion battery materials synthesis and scaling-up from milligram-scale to kilogram-scale is highly challenging. The key challenge is in retaining size-structure-performance correlation at all scales for indigenous technology development. In the project, the objectives are to develop synthesis methods for selected Li-ion battery cathode and anode materials that retain high energy density while delivering high power. The deliverables include preparation of half-a-kilogram of cathode and anode materials that retains about 70% of its 1C rate specific capacity even at 60C rate and a comprehensive characterization of the materials ensuring the repeatability of the synthesis.

Lithium-ion (Li-ion) batteries are inconceivably famous nowadays. We can discover them in most of the portable electronic gadgets namely, laptops, mobile phones and iPods. They are very basic since it is calculated comparatively that they are probably the most significant energy-powered liable batteries that are accessible. These batteries are prevalent on the grounds that they have various significant points of interest over numerous satisfying advantages. They're commonly a lot lighter than different kinds of Li-ion batteries of a similar size. The electrodes of a Li-ion battery are light in weight. On account of Li-ion battery, as fabricated full-cell is in a discharged state, meaning all the lithium ions are hosted in the lattice of the cathode material and the anode that in a state of accepting a number of Li-ions from the cathode. In this way, the batteries should be charged before use and the Li-ion movement direction is reversed during discharge. This oxidation/reduction reaction indicates that materials which can insert and release Li-ions reversibly have the potential to become lithium ion battery electrode materials. More importantly, the cathode materials should have high voltage during reduction (discharge) and the anode should have low voltage for the Li-ion battery to have a high operating voltage. This project is an approach to get a new invention on the power density of Li-ion batteries. Normally, an ordinary mobile phone Li-ion battery can deliver less than 0.5 kW/kg power with respect to the weight of the battery. This project tries to introduce nano-engineered high power Li-ion battery materials (both cathode and anode) that can deliver > 5 kW/kg power. India as a country is aspiring to achieve 100% electric vehicle (EV) sales by 2030, and can rise to become manufacturing hub for batteries [1].

Perhaps the best challenge at present is the manner by which to understand the "low carbon society" in view of the trend setting innovations for reasonable advancement. Electric vehicles is one of the key components included by many countries in their political policies towards climate change. India being one of the largest democratic country in the world with huge population should also be able to contribute significantly based on policies for short-term and long-term consequences. Key objectives for India include, (i) Reduce oil consumption, (ii) Facilitate adoption of clean energy vehicles, (iii) Improve transportation and (iv) Facilitate employment growth are a few to mention [2]. To support the National mission through research, the key innovation for this project is to build the next generation energy storage devices with an excellent power density and high energy density for



hybrid electric vehicles (HEV) and pure electric vehicles (EV). In this regard, significant amount of focus has been on nano-scale materials to enable such energy storage devices by improving all the aspects of lithium-ion batteries. Basic aim of this project is to devise a high power Li-ion battery by engineering the anode and cathode used in the battery. High power batteries are crucial as it will enable a possibility of on-route charging. For example, consider an electric bus with fast charging option, it is highly suitable for local transport rather than inter-state transport. Most of local transport buses round trip is typically 20-30 km range and the time duration available at the end point is nearly 10 min. Though the capacity of the battery is less (which giving only driving range of few tens of km only) with the 10 min charge, the bus can be ready for the next trip.

By and large, nano-scale materials can shorten the diffusion length of Li-ion during the intercalation/de-intercalation process which improves the rate performance of electrode materials. High storage capacity of Li-ion batteries has just prompted their predominance in the portable electronics market. Be that as it may, another level of movement is required for joining high energy and power densities for applications, for example, HEV and EV. To accomplish the objective of Li-ion batteries for new markets, Li-ion electrode materials (cathode and anode) need to have excellent rate capability. Such an excellent rate capability is related to the electronic conduction and the diffusion of Li-ion during the intercalation/de-intercalation process of electrode materials. Advancement of safe, economically competitive and environmentally responsible nano-empowered items is attractive to stay away from unintended outcomes. Given the ecological wellbeing and security vulnerabilities related with nanomaterials, extra precautionary measures might be required, in spite of the fact that not controlled. Organizations working with designed nanomaterials might need to comprehend choice tradeoffs for the expenses related with expanded degrees related to wellbeing and potential natural effects.

LMO has the working potential of about 4.0 V (Vs. Li/Li+) and the theoretical capacity of LiMn<sub>2</sub>O<sub>4</sub> is 148 mAh/g [3–5]. Apart from such advantages, LiMn<sub>2</sub>O<sub>4</sub> suffers from capacity fading when operated at elevated temperatures ( $\geq 50$  °C), which is mainly attributed to Mn<sup>2+</sup> dissolution into the electrolyte through the disproportional reaction given by,  $2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$  and unit cell distortion [6–8]. The unit cell distortion refers to the phase transformation from cubic to tetragonal induced by the Jahn-Teller distortion of Mn<sup>3+</sup> octahedron during lithiation/delithiation of LiMn<sub>2</sub>O<sub>4</sub> [9–11]. As far as Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> anode is concerned, particle size of about 30 nm is considered to be ideal for reversible storage of Li ions as reported by Borghols et al. [12]. Improving the electrical conductivity of the slurry casted electrode can be achieved by 3

compositing high surface area and high aspect ratio carbon nanostructures as additives [13]. Carbon nanotube (CNT) as additive can enhance the rate capability of the electrodes compared to other forms of carbon as evidenced from previous study [13-15]. However, the crucial factor hindering the high rate capability of electrode materials is believed to be the charge-transfer resistance at the electrode/electrolyte interface [16-19]. Full-cell combination of LiMn<sub>2</sub>O<sub>4</sub>-Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> have been reported in the literature however, we report here a high power full-cell Li-ion battery with rate capability and the corresponding specific capacities that are unprecedented [20-23]. This combination has the advantage of being one of the safe Li-ion battery with the potential to be employed for high-end electric vehicle applications [24-25].



Fig.1: (a) 10L Autoclave facility and (b) sol-gel process for the scaled-up synthesis of Li-ion battery materials

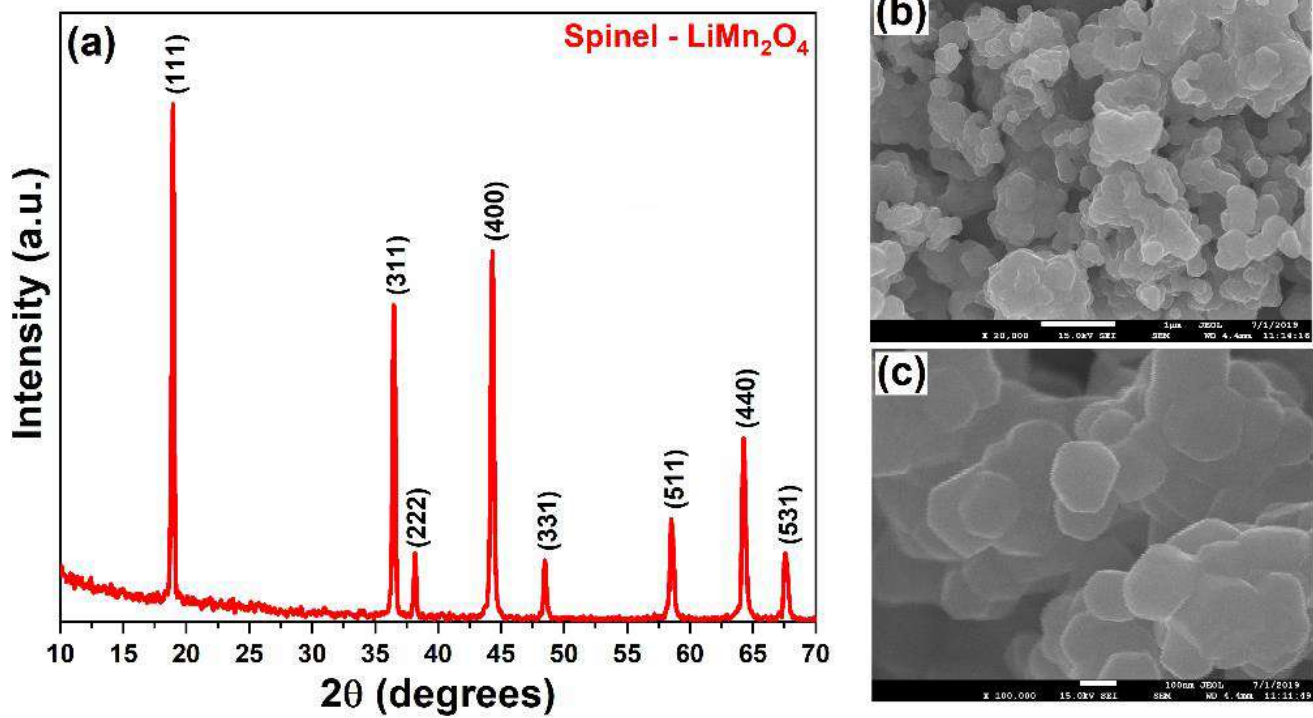


Fig.2: (a) XRD and (b & c) FESEM images of the  $\text{LiMn}_2\text{O}_4$  cathode material

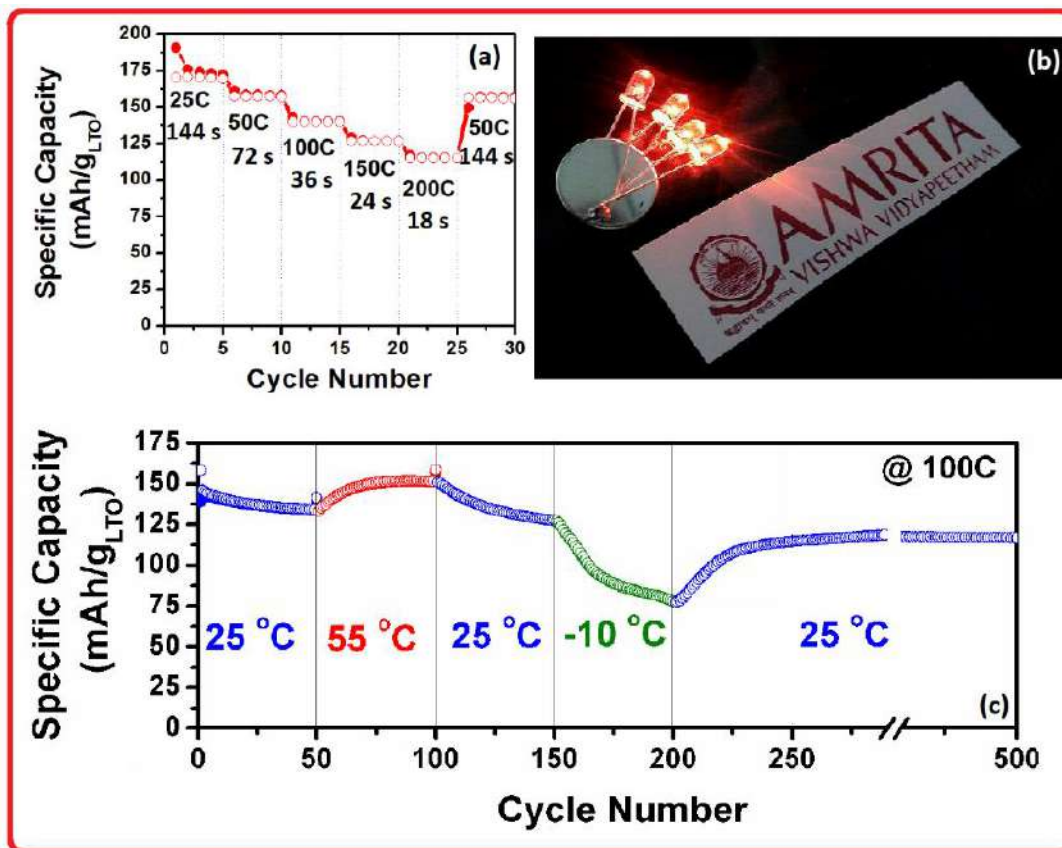


Fig.3: (a) Rate capability of lab-scale full-cell (b) 4-LEDs lit by a single coin-cell and (c) All temperature operation of the full-cell.

The adequacy of the intercalation procedure is dictated by ionic–electronic conductivities, number of lattice locations accessible for Li-ions and density of accessible electronic states around the Fermi level in the electrode materials. Thus, the parameters including voltage of cell, capacity and current density are characterized by properties of electrode materials. As part of this project large-scale Li-ion battery materials synthesis facilities have been set-up in the lab (for 5

example: Fig.1a shows the 10L autoclave facility). The selected materials for scale-up include  $\text{LiMn}_2\text{O}_4$  (cathode) and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (anode). The selection of these materials stem from several aspects including, stability, transition metal abundance (in India) and potential for high power and cycle life. Fig.2 shows the XRD and FESEM images of the  $\text{LiMn}_2\text{O}_4$  cathode material prepared by the sol-gel process described in the supporting information file. Fig.3 shows the lab-scale developed  $\text{LiMn}_2\text{O}_4$ - $\text{Li}_4\text{Ti}_5\text{O}_{12}$  Li-ion battery full-cell performance. Fig.3a shows the rate capability of the lab-scale cell which the time of charge/discharge is indicated which ranges from 144 seconds to as fast as 18 second. To show the high power capability 4 high power LEDs are lit from a single coin-cell (Fig.3b) and the full-cell is demonstrated to operate at a wide range of temperature ranging from  $55^\circ\text{C}$  to  $-10^\circ\text{C}$  (including room temperature of  $25^\circ\text{C}$ ). At present, the cathode material synthesis of up to 100 g has been demonstrated and final phase is to show 500 g. Anode material development to 250 g is under progress and by August 2020, it is expected to deliver both cathode and anode materials of 500 grams to DST. We have also filed two patents based on the cathode and anode materials that are being scaled-up here [26, 27].

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# Electrospun nanofibers as functional materials for lithium-sulfur batteries

Project Reference No. DST/TMD/MES/2K17/73

To meet the demand of future energy needs, development and commercialization of energy dense battery technologies beyond today's lithium-ion batteries are essential. One of most promising candidates is the lithium-sulfur battery, which offer theoretical energy density more than five times that of the state-of-art lithium-ion batteries. Improving the capacity and cycle life of lithium-sulfur batteries by tackling the polysulfide shuttling problem become a measure challenge for the researchers and battery experts across the world. Our group have unveiled a promising breakthrough using electrospun nanofibers as flexible additives for this type of batteries.

Depletion of fossil fuel and intermittency of renewable sources of energy such as wind and photovoltaics could not fulfill the energy need. Rechargeable batteries therefore offer an ideal opportunity to move away from the intermittent sources of energy. The commercially introduction of lithium-ion rechargeable batteries in 1991 heralded a revolution in consumer electronics. The high energy produced with a low weight of lithium-ion battery pack provides an opportunity to engineer a panoply of electronic devices starting from flexible electronics to electric vehicles. Over the years, the battery experts have succeeded in improving the energy density of lithium-ion batteries gradually approaching to theoretical limits and making them more efficient, just by further optimizing the existing architecture. Ultimately, to meet the ever-increasing energy density demand for many future applications, there is a need of innovative alternatives beyond the lithium-ion battery technology. For example, a key consideration for batteries applicable for future electric vehicles and large-scale energy grids are to be small and light weight with much higher energy densities, which are beyond the practical limits for today's lithium-ion technology. Therefore, instead of a step change in lithium-ion battery technology, a completely new electrode chemistry and architectures that have much higher energy density could be an alternative to meet the future energy requirements. In this regard, lithium-sulfur batteries offer promising battery chemistry with up to five times higher energy density than the state-of-art lithium-ion batteries and therefore, considered as the promising next-generation battery technology 1,2.



## How does Lithium-Sulfur battery work?

A lithium-sulfur battery is assembled from lithium anode, sulfur cathode, a separator and electrolyte. During discharging,  $\text{Li}^+$ -ions are moved by an electrochemical driving force from the anode to the cathode through the ionically conducting electrolyte medium. The movement of  $\text{Li}^+$ -ions creates free electrons in the anode that leads to the development of charge. To neutralize the charge, electrical current then flows from anode to the cathode through a device being powered (cell phone, computer, electric vehicle etc.). During charge, the reversible phenomena happens, where the  $\text{Li}^+$ -ions move from cathode to anode. The separator blocks the direct flow of electrons between the electrodes from inside the battery. During the repeated discharge-charge process, the sulfur which is in cyclic octa-atomic state ( $\text{S}_8$ ) undergoes a two-electron redox reaction forming a series of lithium polysulfide intermediates ( $\text{Li}_2\text{S}_x$ ,  $1 \leq x \leq 8$ )<sup>3</sup>. The schematic of a lithium-sulfur battery is shown in Figure 1.

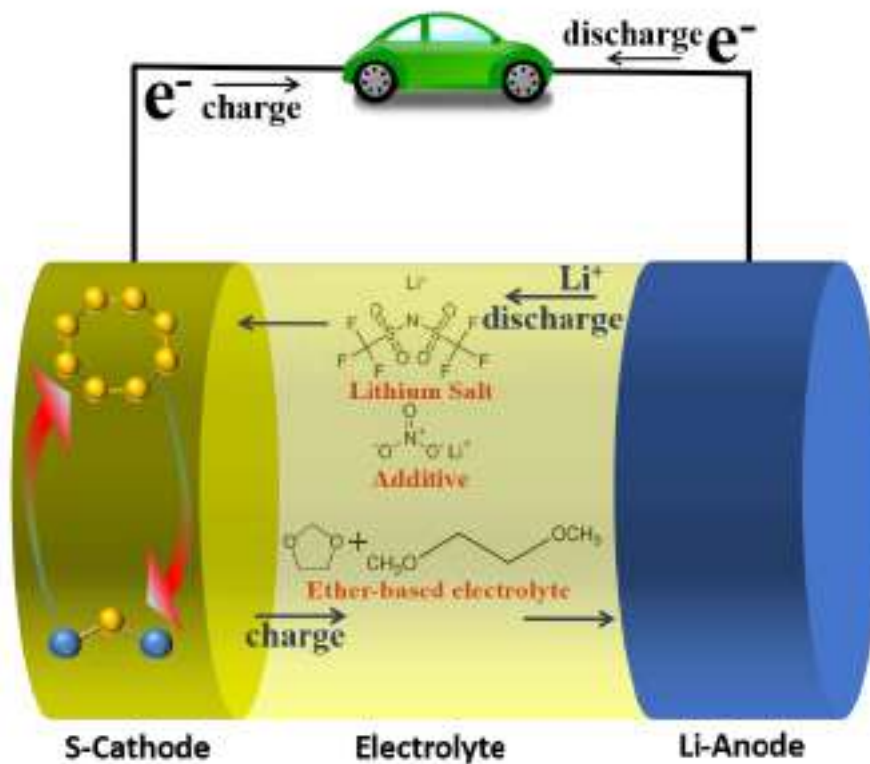


Figure 1. Schematic of a lithium-sulfur battery

## Why Lithium-Sulfur battery is a challenge?

Indeed, sulfur is highly abundant and cheap and environmental friendly, which could make the lithium-sulfur battery technology much more commercially viable, however, the problem with these batteries so far has been their instability, and consequent low cycle life. The insulating nature of sulfur and the intermediate lithium polysulfides formed during cycling along with their morphological and structural changes result in unstable electrochemical contact within the sulfur electrode. This creates a challenge to achieve the capacity near to theoretical limit. In addition, the dissolution of higher of lithium polysulfides ( $\text{Li}_2\text{S}_x$ ,  $3 \leq x \leq 8$ ) in most of the liquid organic electrolytes lead to a fast capacity decay, high self-discharge and low columbic efficiency.

## Electrospun nanofibers for Lithium-Sulfur batteries

The one-dimensional nanofibers fabricated from electrospinning method have received much attention for major components in advanced battery systems<sup>4</sup>. The high specific surface area of electrospun nanofibers provide sufficient reaction sites for dissolved lithium polysulfides and therefore, such nanofibers are widely employed in various components such as cathode, interlayer, separator of lithium-sulfur batteries<sup>5–7</sup>. Recently, our group have developed a novel approach of incorporating electrospun nanofibers as flexible additives in sulfur cathode to hold the lithium polysulfides in position, protecting their dissolution and improving the cycle life of lithium-sulfur batteries<sup>8</sup>. A systematic set of experiments was conducted to fabricate core@shell structured nanofibers of in-situ grown sulfur core embedded inside porous polyacrylonitrile (PAN) shell ( $\text{S@PAN}$ ). The nanofibers were then coated with a thin layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) to obtain conductive channels with a unique co-axial structure (PEDOT- $\text{S@PAN}$ ). The improvement in electrochemical performance of lithium-sulfur batteries such as capacity, cycle life, rate capability etc. by the incorporation of PEDOT- $\text{S@PAN}$  nanofibers in cathode was confirmed by various electrochemical test in a coin-cell configuration. The overview of the work is shown schematically in Figure 2. Our group is working to further improve the nanofibers architectures for lithium-sulfur batteries and enable its future commercialization. The focus is on to incorporate novel functionalities in the nanofibers such that it can further help in improving the capacity as well as capacity retention of the Lithium-Sulfur batteries

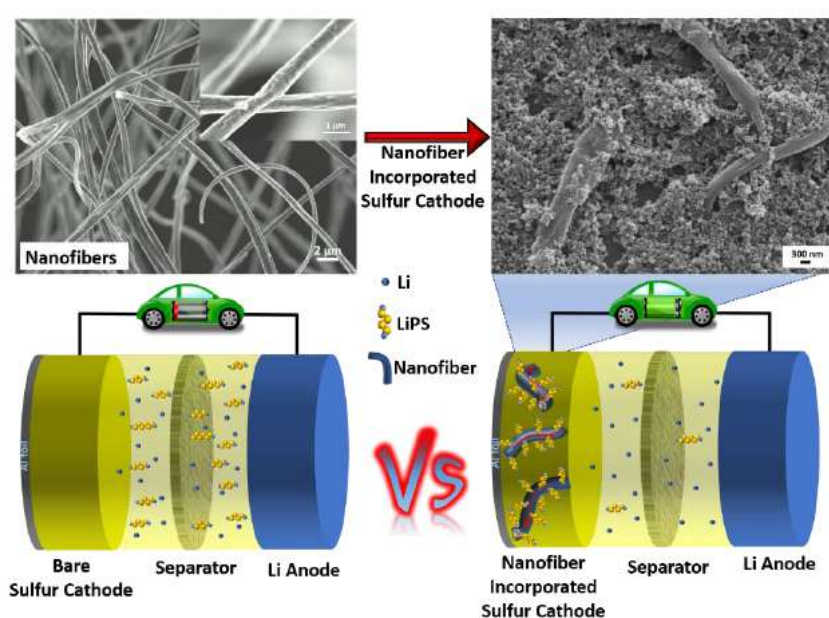


Figure 2. Electrospun nanofiber incorporated cathode to improve the performance of lithium-sulfur battery.

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# 11


## Development of new Mg-S battery chemistry and electrodes through synthesis characterization and simulations

Project Reference No. DST/TMD/MES/2K17/66

Magnesium (Mg) Batteries has attracted lot of attention over the last few decades because of high theoretical volumetric capacity, safety, economically viable and abundance of material. The amalgamation of sulfur cathode with the Mg anode is the best combination for future battery applications because of its high theoretical energy density, non-toxicity, natural abundance, and low cost. But still the electrochemical performance of the cell is not satisfactory because of several reasons. One reason is the usage of the metallic magnesium which in turn leads to the formation of a passive layer (nonconductive) on the anode while charging and thus, inhibiting cycle performance. This passive layer is the result of the decomposition of electrolytes on anode during Mg ion reduction. This calls for the development of a suitable electrolyte which should be chemically compatible with the electrophilic sulfur and is also capable of reversing Mg deposition/dissolution. The inclusion of sulfur cathode also involves certain drawbacks including the dissolution of polysulfide, shuttling effect, low active material utilization and fast capacity fading. In this MES Project we mainly focused on the cathode material and attempted to reduce the problems associated with the usage of sulfur cathode by synthesizing sulfur nanoparticles and further coating with the different types of conductive polymers. This newly developed cathode material is currently undergoing tests to verify its electrochemical performance against Mg metal anode.

Battery technology is the most promising renewable energy and emission free technology. Since the invention of Lithium ion battery (LIB), it has played a very crucial role in consumer electronics and automobile industry. With over two decades of research on materials and engineering on cell design, the energy density of LIBs has reached 240 Wh kg<sup>-1</sup> and 670 Wh L<sup>-1</sup> at the cell level [1]. In rechargeable battery market, LIBs occupy a supreme position because of its stable electrochemistry and long cycle life [2] but Lithium-Sulfur (Li-S) battery is having greater chances of replacing LIB in the near future because of its high theoretical energy density (2600 Wh kg<sup>-1</sup>), which is about four to five times higher than that of LIBs [3]. Therefore, there is a need to carry out research on the Li-S batteries to achieve high theoretical energy density potential in applications such as military power supply and aviation sector. Nevertheless, Li-S batteries are not flawless; they also have certain disadvantages such uncontrollable formation of Li dendrites which can penetrate through the separator and can make contact with the cathode (Battery shortage) [4]. In addition, the Li dendrites can detach from the anode and remain as dead Li in the battery further diminishing the cycle life and specific capacities [5]. Furthermore, the polysulfide dissolution can result in passive layer formation, thereby, deteriorating the performance of Li-S Battery [4].

To avoid the problems associated with Li-S batteries, Toyota Motor Corp. in 2011 for the first time introduced rechargeable Mg-S batteries [6]. Usually, Mg-S battery works with redox reactions (Figure 1a) and during the course of battery discharge, Mg anode gets oxidized and becomes Mg<sup>+2</sup> by releasing two electrons. This Mg<sup>+2</sup> ion migrates to cathode through electrolyte and separator. At cathode the sulfur reacts with Mg<sup>+2</sup> ion and forms long chain polysulfide, followed by the formation of short chain polysulfide and finally forms MgS. The electrons passes from the anode to cathode through the external electrical circuit. Ideally, during charge, Magnesium polysulfide reoxidizes and forms Mg<sup>+2</sup> ion and Sulfur. This sulfur remains at the cathode, however, Mg<sup>+2</sup> travels back to



the anode. Mg-S batteries have more advantages when compared to LIBs such as the formation of dendrites in Mg-S batteries is quite rare, hence, reinforcing higher battery safety. Another advantage is that both Mg and Sulfur are highly abundant and Mg-S battery also has higher theoretical volumetric capacity than Li-S batteries (2062 vs 3832 mAh cm<sup>-3</sup>) due to divalent nature of Mg<sup>+2</sup> [7]. These benefits enhance the interest of researchers to further explore the usage of Mg-S batteries. Figure 1. b) and Figure 1. c) depicts an increasing trend in the research of Mg batteries and Mg-S batteries.

## Anode material

Anode is the important part in the Mg-S battery. During cycling the electrolyte reacts with the anode and forms a passive layer on the anode which is resistant to the diffusion of Mg ion. This affects the life of the battery. But the anode in Mg-S batteries has grabbed little attention than electrolyte and cathode. Normally metallic Mg is used as the anode material in forms of foil, discs, ribbons and plates in Mg batteries. But the metallic Mg has very less surface area. To increase the surface area, the Mg powder is ball milled with graphite powder further forming a pellet by using a hydraulic press [12]. Two different pressures i.e. 75 and 350 MPa were used to form the pellet. According to the article [12], the less pressed anode is showing better performance than the highly pressed anode and Mg foil. This better performance was attributed to the high porosity of the less pressed anode allowing the soaking of electrolyte within the anode. The ohmic contact resistance between the current collector-anode and electrolyte-anode is low in case of the less pressed anode (Nyquist plot,  $P_g$ ) [12]. Another key observation was that the powder anodes ran for 100 cycles whereas the metallic Mg foil only ran for 15 cycles.

## Separator

A separator is placed between the anode and cathode to avoid the electrical shortage between the two but it allows for free transportation of ions through it. Glass fiber sheets and micro porous polymer membranes are two most commonly used commercial separators in Mg-S batteries. In Mg-S batteries, the utilization of sulfur and diffusion of polysulfide are of concern. To overcome this, very recently a modified separator has been used in Mg-S batteries [13]. In this process the separator cathode side is coated with Carbon nano fibers (CNF) by using vacuum filtration. Consequently, the sulfur is coated on the CNF and again sandwiched with CNF. When it was tested electrochemically, the cell coated with CNF shows 950 mAh g<sup>-1</sup> capacitance at first cycle and capacitance remained at 800 mAh g<sup>-1</sup> after 20 cycles. But the uncoated one showed 1000 mAh g<sup>-1</sup> at first cycle and dropped to 200 mAh g<sup>-1</sup> after 20 cycles. This improvement is due to enhanced sulfur utilization of cathode material as induced by conductive CNF coating and trapping of polysulfides.

## Current collector

The current collector also plays a vital role in Mg-S battery. Normally copper foil, alumina foil, stainless steel, nickel foil and carbon coated alumina foil are used as a current collector. But copper is unstable in chloride containing electrolyte. Other than these commercial current collectors N,S-Dual doped carbon cloth is synthesized and used in this MES project as a current collector for Mg-S batteries [14]. Solvothermal synthesis technique was implemented to create this doping. In case of doping, the cell specific capacity was 388 mAh g<sup>-1</sup> after 40 cycles whereas the normal carbon cloth cell ran for only 10 cycles at 0.01 C. This improvisation was the result of an increment in conductivity due to doping and this doping also served as a reservoir to hold the polysulfides. The results are shown in Figure 2.

## Electrolyte

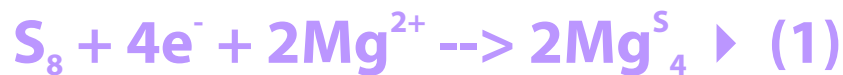
Ideally, an electrolyte should have high ionic conductivity, chemical stability, electrochemical stability, and thermal stability, low toxicity, low flammability and wide voltage window. For Mg-S batteries, more research is intended for the electrolyte. Almost all the traditional electrolytes are nucleophilic electrolytes and incompatible with sulfur material. So the modifications have to be done in these electrolytes to make it compatible with the sulfur material and new non-nucleophilic electrolytes have to be synthesized and

test for suitability in the Mg-S batteries. For the first time in 2017, the nucleophilic electrolyte (all phenyl complex) was used in Mg-S battery in the research of new cathode material [15] because of its high oxidative stability against Mg (3.2 V. the cell ran for 36 cycles). In 2017, another research group explored the use of copper as a current collector with the all phenyl complex-based nucleophilic electrolyte to avoid the usage of stainless steel as current collector but the performance was not reported satisfactory. The reason being that the cell ran for 20 cycles with the last cycle specific capacity being 100 mAh g<sup>-1</sup>. But with minor addition of Lithium Chloride to the electrolyte, the cell performance increased to 40 cycles with the last cycle specific capacitance 300 mAh g<sup>-1</sup> at 0.005 C [16]. After that the same research group used (PhMgCl)<sub>2</sub>-AlCl<sub>3</sub>/ tetrahydrofuran-based nucleophilic electrolyte in Mg-S battery and ran cell for 200 cycles at a rate of 0.1 C [17]. The first cycle capacity was 979 mAh g<sup>-1</sup> and the 200th cycle capacity was 368.8 mAh g<sup>-1</sup>.

The non-nucleophilic electrolytes are more compatible with the electrophilic nature of sulfur cathode. That is the reason lot of research is going on in the non-nucleophilic electrolytes in the Mg-S batterie [6], [7], [18]–[29].

## Cathode

Sulfur is the cathode material for the Mg-S batteries. Sulfur is abundant, nontoxic, and has high theoretical energy density (1675 mAh g<sup>-1</sup>). Normally in Mg-S battery, sulfur participates in electrochemical reactions by oxidation and reduction (Conversion). When these redox reactions take place, the polysulfides form. The electro chemical reactions are mentioned below [26]. The first reaction is signed with equation 1.



The second step is assigned to a liquid–solid two-phase reduction from MgS<sub>4</sub> to MgS<sub>2</sub>



The final step entails the reduction of MgS<sub>2</sub> into MgS



The polysulfides diffuse towards anode and cause the loss of active material, finally resulting in capacity fading and poor cycle life. To avoid this glitch, sulfur is accommodated in high surface conductive carbon. This carbon should have high conductivity, high interaction between carbon material and sulfur, high interaction between carbon material and polysulfide, and high mechanical stability to withstand the volumetric change emerging in the cell during charge and discharge. The commonly used carbon materials are CMK-3, carbon nanotubes, carbon nano fibers and rGO. Extensive research is being carried out on cathode materials [15], [17], [19], [26], [30], [31] to increase the cycle life of Mg-S battery. As part of the MES project, we are making sulfur nanomaterial composites with different carbon additives and coating with different conductive polymers. Overall, the cell processing steps from synthesis to cell making and electrochemical analysis are shown in Figure 3.

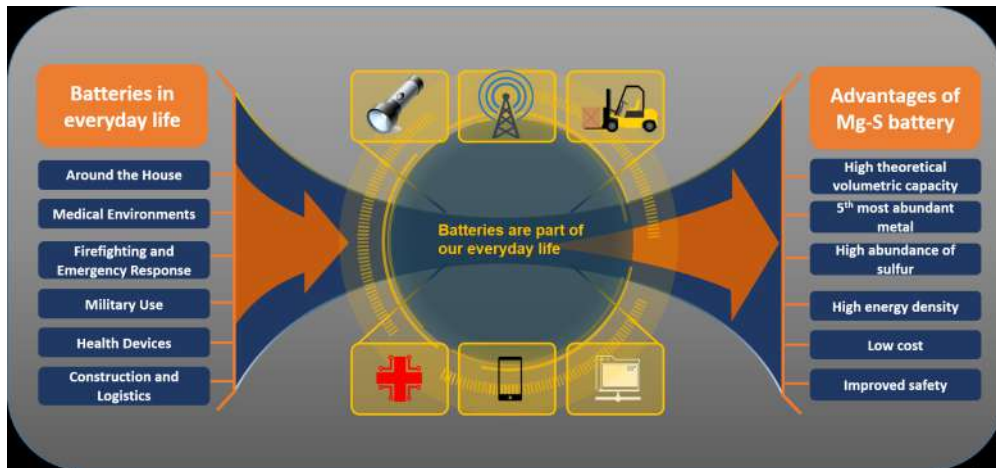


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# Figure file



Graphical abstract



Figure 1. a) Schematic diagram of Mg-S battery working mechanism, b) Number of research articles published on Mg Batteries since 1998, c) Number of research articles published in Mg-S batteries (Till now).

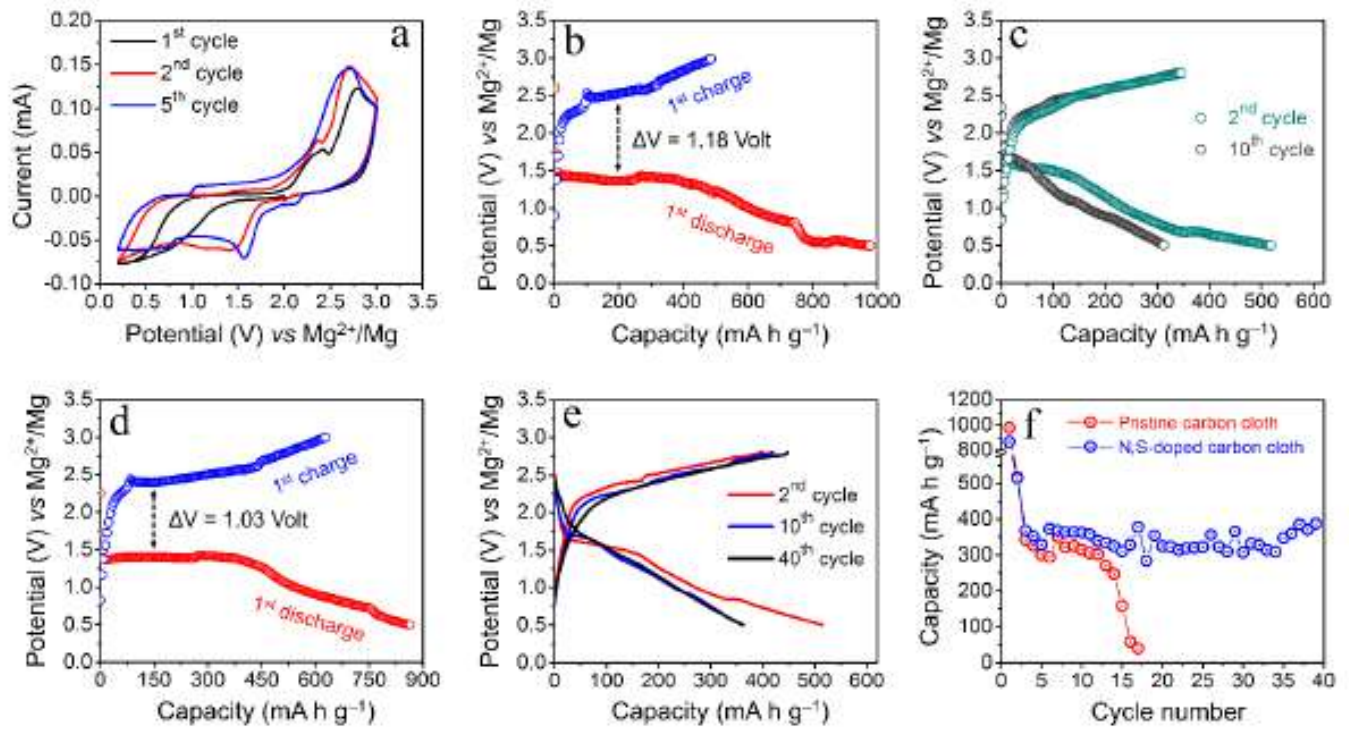


Figure 2. (a) Cyclic voltammograms of S/rGO@DCC cathode. (b) First cycle charge-discharge profiles of S/rGO@PCC cathode at 20 mA g<sup>-1</sup>. (c) Charge-discharge profiles for the 2nd and 10th cycles of S/rGO@PCC cathode at 20 mA g<sup>-1</sup>. (d) First cycle charge-discharge profiles of S/rGO@DCC cathode at 20 mA g<sup>-1</sup>. (e) Charge-discharge profiles for the 2nd, 10th and 40th cycles of S/rGO@DCC cathode at 20 mA g<sup>-1</sup>. (f) Comparison of discharge capacity vs cycle number between S/rGO@PCC and S/rGO@DCC cathodes at 20 mA g<sup>-1</sup>. (Sulfur/rGO composite, DCC-Dual doaped carbon cloth, PCC-Pristine carbon cloth).

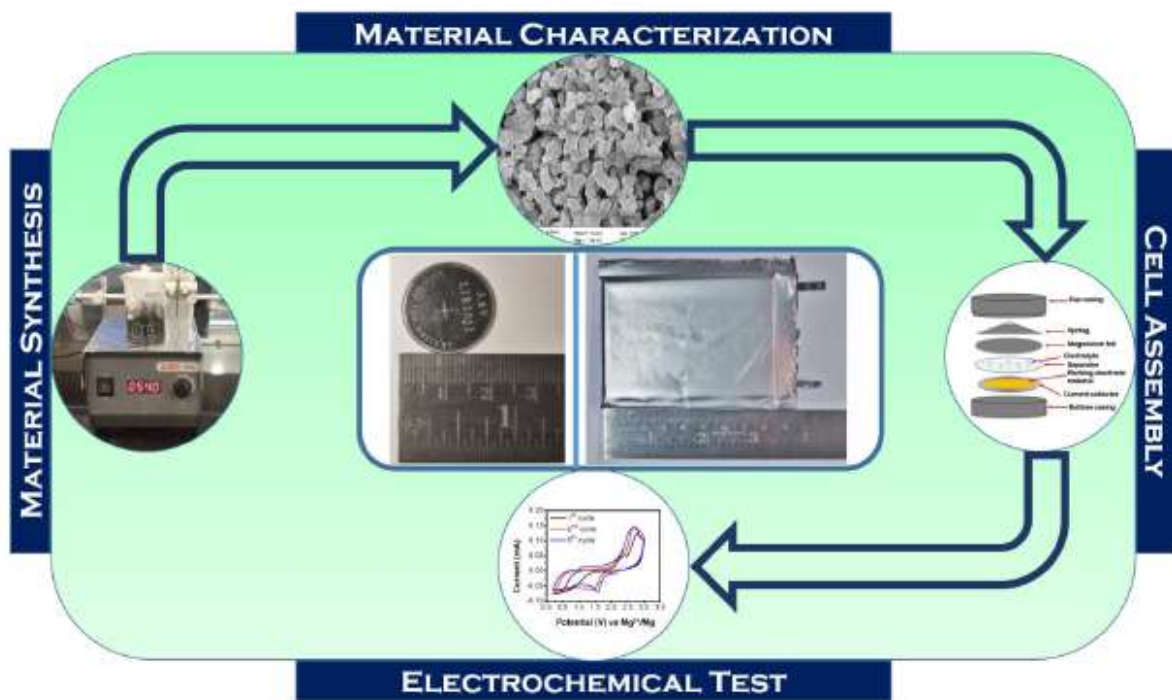


Figure 3. Processing steps in cell making from synthesis to electrochemical analysis

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# 12

## Development of functional phase change material for cool thermal energy storage applications

Project Reference No. DST/TMD/MES/2K16/98

Global energy demand has been increasing exponentially due to growth in population, rapid urbanization and industrialization, leading to a multi-fold increase in the consumption of fossil fuel. The enormous usage of fossil fuel results with the unprecedented climatic changes, receiving much attention on improvement in the overall efficiency of the system. Buildings are highly energy intensive sectors, consuming nearly 40 % of world's total energy and utilizing a major portion of this for space cooling applications<sup>1</sup>. There has been a pressing need to reduce energy consumption in buildings and integration of Cool Thermal Energy Storage (CTES) system is the most viable option to significantly reduce the energy consumption. Water is being used as a potential Phase Change Material (PCM) in the CTES systems, owing to its excellent thermal properties, and ease of handling. However, subcooling of water demands a lower operational temperature of the evaporator, consuming an additional energy of 3 - 4 % per degree temperature drop<sup>2</sup>. Considering the above challenges, present research work aims to reduce or eliminate the subcooling behavior of water with dispersion of Natural Graphite Flake (NGF) and investigate its charging characteristic in a spherical glass capsule.

Functional Phase Change Material (FPCM) is prepared with De-Ionized (DI) water as the base PCM and NGF as the additive, Polyvinyl Pyrrolidone (PVP) as surfactant through two-step method, as illustrated in Figure 1. Initially, a required mass of NGF (1 wt. %) and PVP (20 wt. % of NGF) is taken and mixed with a known volume of base PCM. This mixture is subjected to stirring for 15 min, followed by a probe sonicating at 20 kHz for 90 min to disperse the NGF uniformly. After keeping the prepared FPCM for 72 h idle, the size of dispersed NGF is analyzed using a scanning electron microscope (SEM) and it is found to be between 1- 2.5  $\mu\text{m}$ . The prepared FPCM is poured into a borosilicate spherical glass capsule of '62 mm size with '1 mm' wall thickness, located with three Resistance Temperature Detectors (RTDs) as shown in Figure 2. Solidification characteristic of the FPCM is performed by placing the capsule containing FPCM in the center of a rectangular insulated chamber, filled with an aqueous mixture of ethylene glycol (60:40 by volume) as the coolant. The coolant temperature is maintained at  $-7^\circ\text{C}$  using a chiller unit and the photographic image of the experimental test-rig is shown in Figure 2.

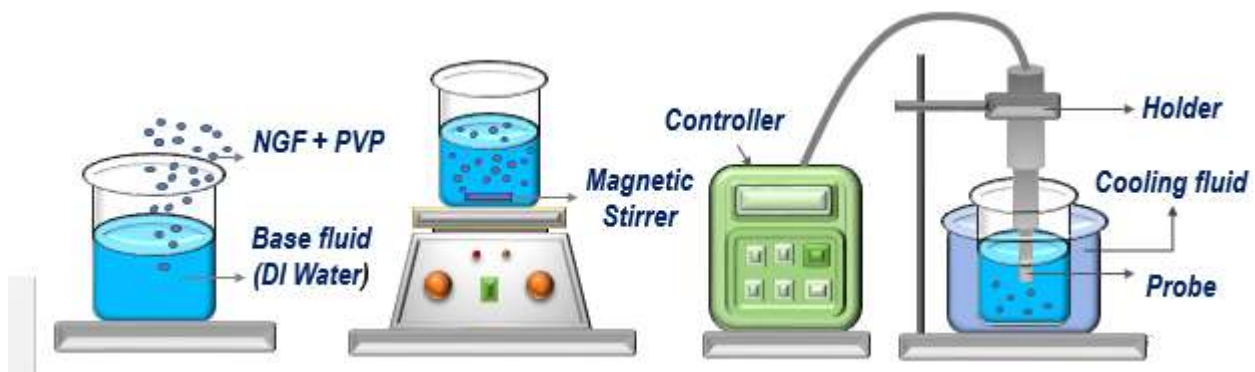


Figure 1 Preparation of FPCM

During solidification, base PCM undergoes the subcooling upto  $-5.4\text{ }^{\circ}\text{C}$  in the metastable liquid region and the onset of solidification occurs at  $1.4\text{ }^{\circ}\text{C}$  throughout the PCM volume, showing the homogenous nucleation behavior. As could be seen Figure 3, Time taken between the onset and end of solidification is '73 min' at the center of the capsule. Astonishingly, the subcooling is eliminated in the FPCM due to creation of more nucleation sites in presence of NGF through a reduction in volumetric free energy. In addition, a reduction in the solidification duration of 12.5 % has been observed, compared to the base PCM. The inherent higher thermal conductivity of NGF and subcooling elimination are the major reasons for the above reduction. As can be noticed, 94 % of the base PCM volume gets solidified in 77 % of total solidification duration and remaining 6 % volume solidifies in 23 %

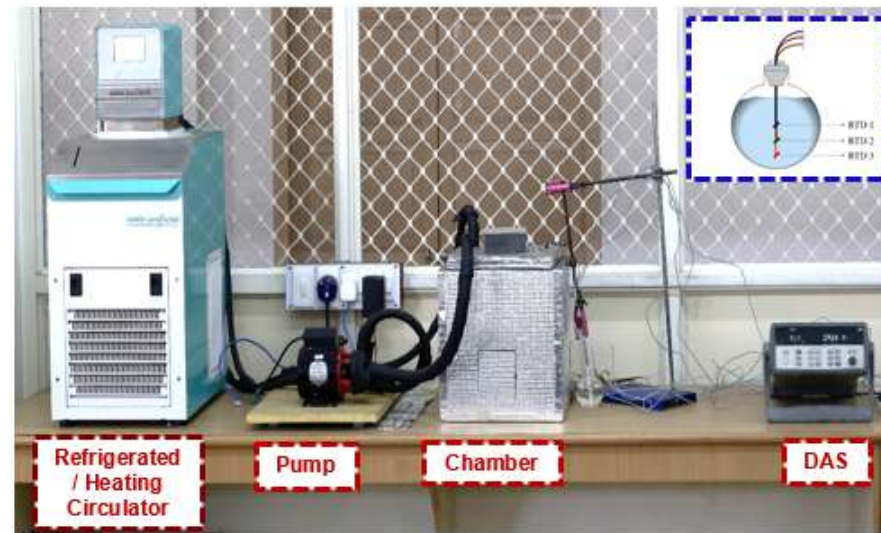


Figure 2 Photograph of the experimental facility

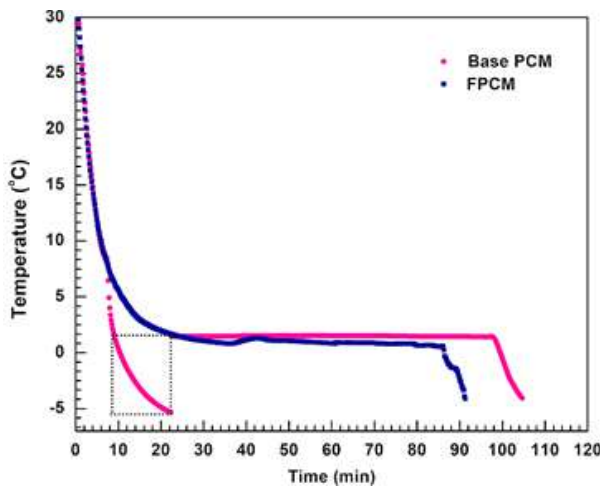
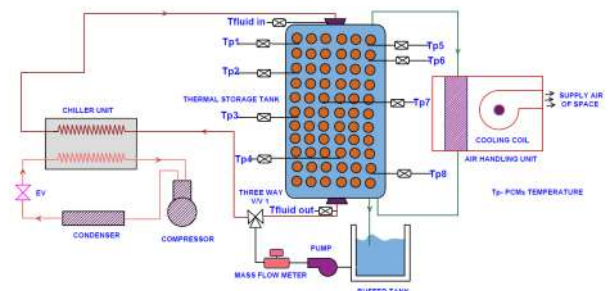


Figure 3 Charging behavior of FPCM

of total solidification duration under decelerated mode. This results with an undesirable energy consumption by the chiller unit, making to turn off the chiller during the decelerated mode of charging. For the FPCM, 94 % of the volume is solidified at a faster rate of 10.5 %, compared to base PCM. Based on the above discussion, the combined effects of subcooling elimination, shortened solidification duration and partial charging in accelerated mode make the FPCM as a potential energy storage material in the CTES applications. To explore the energy saving opportunities using the FPCMs, a pilot scale CTES system is developed and integrated with a refrigeration system of 18 kW capacity as shown in Figure 4. The system is installed at 'Center for Student Affairs, Anna University, Chennai' and the experimental trials are under progress.



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# 13

## Enabling the development of Na-ion batteries

Project Reference No. DST/TMD/MES/2K17/13

Na-ion batteries, as an upcoming electrochemical energy storage system, is very important in the contexts of lower cost and widespread availability of Na-sources, as compared to the Li-ion batteries. The above renders it even more important for countries like India, which has abundant sources of Na (but nearly negligible sources of Li). However, one of the major issues associated with the Na-ion battery system is the inability of graphitic carbon (the workhorse anode material for Li-ion system) to intercalate Na-ion. Hence, the first challenge is to develop an alternate anode material, ensuring no compromise on the stability and safety aspects. In this context, Na-titanate ( $\text{Na}_2\text{Ti}_3\text{O}_7$ ) is a promising and safe anode material, but lacks in terms of cyclic stability. Hence, one of the primary objectives is to understand the causes for the cyclic instability and address the same in significant terms. The other concern is related to the development of stable and high capacity cathode material. In this context, sodium transition metal (layered) oxides are potentially capable of being used as a high capacity cathode material, but their practical usage is plagued by the occurrences of numerous phase changes during Na-extraction/insertion, volume changes; while additionally being sensitive to moisture. Hence, the other focus is to develop air stable, high energy density cathode material. Successfully achieving the two objectives will, eventually, render the development of stable and safe Na-ion cells, possessing practically usable energy and power densities.

Transitioning to renewable energy across society will require many changes, including more batteries. Energy storage is crucial for making sure that inconsistent renewable sources, like wind or solar, can stay humming even when the weather isn't going their way. Production and storage of energy have become the most vital issues concerning today's world. Present challenges for batteries are of twofold. In the first place, the increasing demand for powering portable electronic devices and zero-emission vehicles stimulates research towards high energy and high voltage systems. In the second place, low cost batteries are required in order to advance towards smart electric grids that integrate discontinuous energy flow from renewable sources, optimizing the performance of clean energy sources [1]. Taking into account the present day climate conditions (especially in India) and never ending demand for electricity leading to increase in depletion of fossil fuels, seriously impact levels of greenhouse gases like  $\text{CO}_2$ , CO etc. Indian Government as in itself have also taken an initiative of electrification of all gasoline-run vehicles by 2030 [2].

However, Li-ion batteries have their own problems due to the unavailability of lithium and safety issues. It is thus imperative to look for new and abundantly available electrode materials. The relative abundance of lithium in the Earth's crust is limited to be only 20 ppm. In contrast, sodium resources are almost ubiquitous and is also regarded as one of the abundant element in earth's crust, in addition Na only seconds to Li in terms of size and a comparable standard reduction potential which makes it a better alternative for Li-ion battery systems. In spite of the lower energy density and voltage of Na-ion based technologies, they can be focused on applications such as electrical grid storage [3]. The most explored cathodes for sodium ion batteries are layered oxides, Ironically the Na layered transition metal oxides which can reversibly host Na ions are more in number than its Li counterparts, which actually gives

a broader play ground in the chemical space to explore and optimise, for them to make its way through commercial penetrance. Sodium based transition metal oxides as the host lattice for the reversible Na-ion intercalation were first studied in 1980s, which shows that reversible Na insertion can be possible in seven layered transition metal oxides:  $\text{Na}_x\text{TMO}_2$  (TM = Ti, V, Cr, Mn, Fe, Co, Ni) [4]. This is in sharp contrast to their Li counterparts. After an enormous research effort by many researchers, they could develop considerably good number of layered Na-TM oxides which can approximately match up with their Li counterparts in terms of energy density, for example an O3-type (where Na-ion is in octahedral site and there are three TM-O6 stackings in unit cell) mixed transition metal oxide  $\text{Na}(\text{Mn}_{0.25}\text{Fe}_{0.25}\text{Co}_{0.25}\text{Ni}_{0.25})\text{O}_2$  delivers 578 Wh/kg and an O3 type single transition metal oxides  $\text{Na}_x\text{MnO}_2$  reaching capacities of nearly 200 mAh/g. Sodium layered transition metal oxides suffer multiple phase transformations during cycling which results in large no. of plateaus, these plateaus are more significant in single transition metal oxides such as  $\text{NaNiO}_2$ ,  $\text{NaMnO}_2$  and  $\text{NaVO}_2$  etc. These plateaus may be because of two reasons, Na-vacancy ordering and gliding of oxide layers. O3-type sodium transition metal oxides can transform from O3 to P3 during Na-extraction via multiple intermediate phases [5].

The search for suitable anode material poses a fresh challenge on research community since graphite; commonly used anode for lithium ion batteries cannot intercalate sodium as thermodynamics forbids it. This rules out the possibility of graphite being used as anode and opened up various choices, but finding out the “best one” is always difficult. So carbonaceous materials, metal alloys and oxides have been extensively studied as potential anodes for Na-ion batteries. Hard carbon, a popular candidate among the carbonaceous materials, induces serious safety concerns as the redox voltage is close to that of sodium plating [6, 7]. The major drawback of alloying materials is the huge volume change during alloying and de-alloying which cause structural degradation, leading to rapid capacity fade [7].

Among the sodium titanium oxides,  $\text{Na}_2\text{Ti}_3\text{O}_7$  is a promising anode material due to its low but safe redox potential ( $\sim 0.3$  V vs. Na/Na+) [8], low activation energy ( $\sim 0.186$  eV) for diffusion of sodium ions [9] and a decent theoretical capacity (177 mAh/g). However, the major issue pertaining with this material is the cyclic instability and various research groups have been trying to figure out the underlying cause(s) and mitigate the same [9-13].

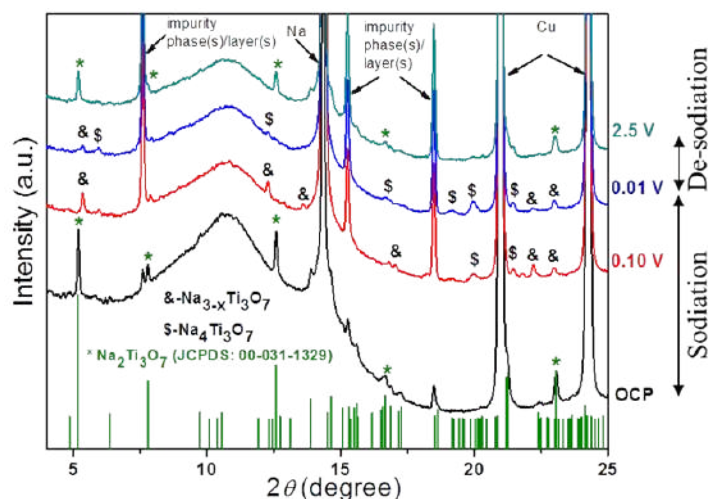


Fig. 1. In-situ synchrotron XRD scans showing the reversibility of  $\text{Na}_4\text{Ti}_3\text{O}_7$  and the formation of impurity phase on  $\text{Na}_2\text{Ti}_3\text{O}_7$  (i.e., NTO) when inside Na 'half cells' (as published in ref. [14]).

One of the major hypothesis regarding the rapid capacity fade of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> was the structural instability of fully sodiated phase Na<sub>4</sub>Ti<sub>3</sub>O<sub>7</sub> [10], but later it was proved via first principle calculations that Na<sub>4</sub>Ti<sub>3</sub>O<sub>7</sub> is stable and Na-insertion in Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> is completely reversible [11]. The in-situ synchrotron XRD studies also ruled out the possibility of irreversibility or structural instability of Na<sub>4</sub>Ti<sub>3</sub>O<sub>7</sub> as the cause of capacity fade (see Fig. 1) [14]. Other hypothesis regarding capacity fade is that it can be probably related to surface/side reactions, including reactions of the Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> with electrolyte. The presence of few unidentified peaks in the in-situ synchrotron XRD (see Fig. 1) also points towards the latter, which was later verified by ex-situ EIS (increase in charge transfer resistance (R<sub>ct</sub>) after charge-discharge; also, 550% increase of initial R<sub>ct</sub> was observed after 10 days even without applying any current), Raman spectroscopy (shift in Raman peaks of the electrodes after 100 cycles). All these observations points that, cyclic instability in Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> stems not primarily from the concerned Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> phases (Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>, Na<sub>3-x</sub>Ti<sub>3</sub>O<sub>7</sub>, Na<sub>4</sub>Ti<sub>3</sub>O<sub>7</sub>) being electrochemically/structurally inactive or unstable. The possible reasons can include loss in electrical connectivity due to the formation of passivation layer upon chemical reaction of the electrode with the electrolyte, which hinders electrochemical Na-uptake/release. The in-situ synchrotron XRD studies indicate the formation of 'new'/impurity phase(s) with irreversible increase in content which is likely to be consisting of lesser Na-containing Na-Ti-oxide compound(s) upon exposure of the Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> based electrodes to the electrolyte.

Incorporation of conducting reinforcements like multi walled carbon nanotubes (MWCNTs) is a promising way to address these issues concerning Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>. It improves the rate capability of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> which is due to poor electronic conductivity (see Fig. 2). Similar EIS and Raman studies on as prepared and cycled Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>/MWCNT shows the increase in R<sub>ct</sub> after 50 cycles is much lesser compared to Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> (i.e., increase in R<sub>ct</sub> suppressed by more than an order of magnitude, in the presence of MWCNTs) and fairly similar Raman spectra even after 100 cycles. Also, upon holding the R<sub>ct</sub> increased for up to 3 days and settled down after with an increment of 270% (while the increase was monotonous for Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>). Correlation of all these results indicates that the wrapping MWCNTs alleviates the negative impacts of formation of insulating 'impurity' phases/layers upon reaction with the electrolyte, which is considered to be one of the reasons for rapid capacity fade. Also, it improves the cyclic stability considerably (~78% capacity retention after 50 cycles compared to ONLY ~6% in Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>) by preserving the mechanical integrity and connectivity (see Fig. 3) [14].

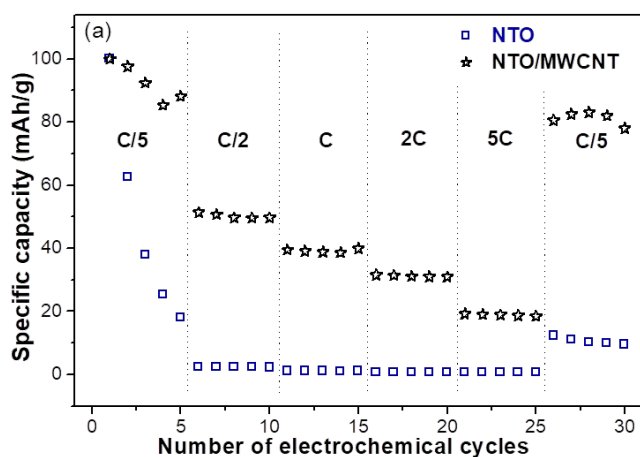


Fig. 2. Variations of the reversible or desodiation capacities (as % of the maximum capacity obtained at ~C/5) with current densities (i.e., C-rates) for both the NTO/MWCNT and NTO, showing significantly improved rate capability in the presence of MWCNTs (as published in ref. [14]).

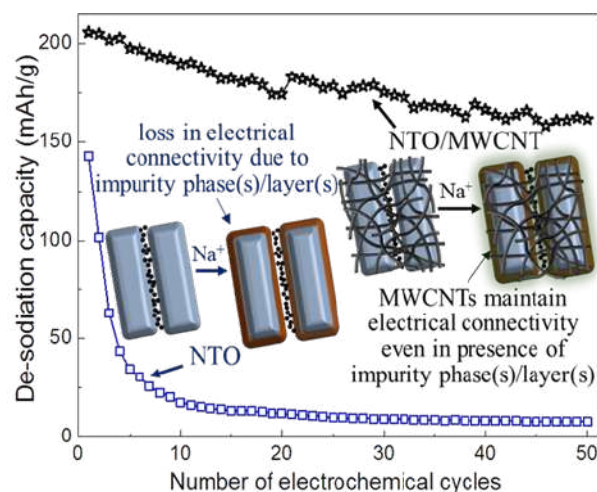


Fig 3. The variations of the reversible (i.e., charging or desodiation) Na-storage capacities with cycle number for NTO and NTO/MWCNT-based electrodes (as published in ref. [14]).

Layered transition metal oxides, which was used as cathodes in Li-ion batteries can also be used in Na-ion batteries but the major problem associated with these materials is they suffer multiple phase transformations during cycling resulting in large no. of plateaus and steps. However, the steps/plateaus during cycling were undone by partial substitution with non-transition metals and transition metals which yields a relatively smooth profile. And one of the most important challenge that sodium transition metal oxides present is the poor air/moisture stability. Most of the transition metal oxides are hygroscopic and air-unstable. Again many reports have been published stating that alloying additions suppressed the water intercalation into lattice, but the systematic mechanistic study was not conducted to understand the air/water stability. In our ongoing work, we tried to synthesise the recently published material  $\text{Na}[\text{Li}_{0.05}\text{Mn}_{0.5}\text{Ni}_{0.3}\text{Cu}_{0.1}\text{Mg}_{0.05}]\text{O}_2$  which leads to a reversible capacity of 172 mAh/g at 0.1C and capacity retention of 70.2% after 1000 cycles at 20C, but during cycling Mn is seen to convert from +4 to +3 which is a Jahn teller active state resulting in structural degradation of material [15]. Against this backdrop we are presently trying to replace the Mn with other transition metal(s) to avoid the occurrence of the distortion associated with  $\text{Mn}^{3+}$ . The same is also tuned to improve the resistance against moisture uptake and associated degradation.

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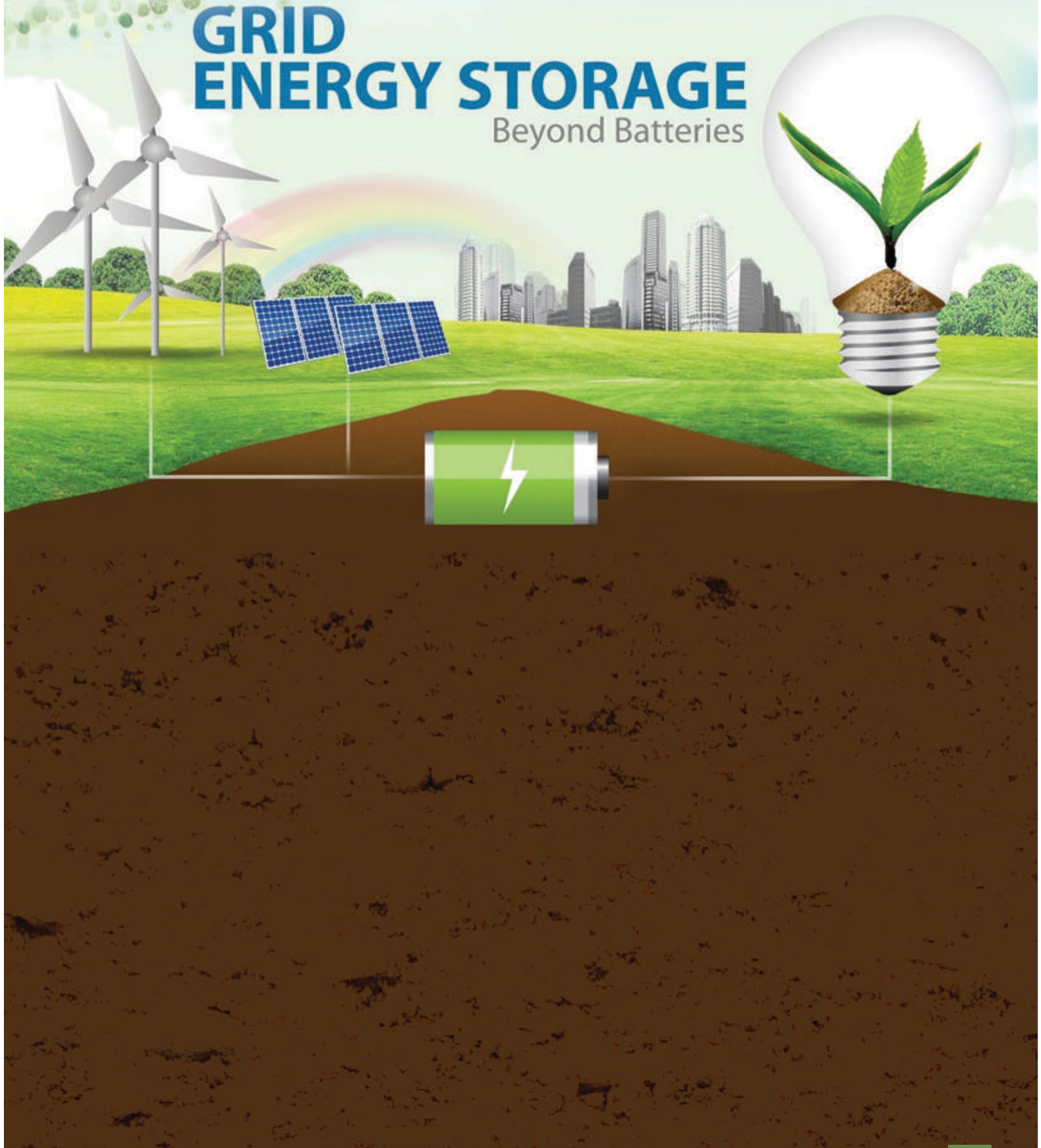
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# GRID ENERGY STORAGE

Beyond Batteries



Petroleum, coal, and other hydrocarbon-based fuels accounted for nearly 90% of India's energy production. Burning these fossil fuels and hydrocarbons causes environmental pollution. Also, petroleum import bears a heavy burden on India's economy. Thus, India is heavily investing on renewable energy sources. Unfortunately, nearly 65% of all utilized energy is being lost as wasted heat. 'Waste heat' is the inevitable heat loss from our electrical appliances – ranging from small home appliances like fridge, laptop, and mobile devices to exhausts of automobiles to large scale industrial sectors like chemical, thermal, steel, cement, and nuclear power plants. Thermoelectric materials, being able to do immediate and reversible conversion of wasted heat into electricity without any moving parts, are believed to be a key answer for the future energy management applications.

The thermoelectric effect is the direct conversion of temperature differences to electric voltage and vice versa. The term "thermoelectric effect" encompasses three separately identified effects: the Seebeck effect, Peltier effect, and Thomson effect. The Seebeck effect which is the conversion of temperature difference to electricity was first discovered in 1821 by the German physicist Thomas Seebeck. Though thermoelectrics is known over 200 years, it took almost a century from the discovery of the effect to initiate the research in this field. At the beginning of the 20th century, thermoelectric materials were extensively studied for applications in civilian and military use. NASA have also used Radioisotope Thermoelectric Generators (RTG) to power their space craft in deep space mission for last 35 years.

For practical applications, a thermoelectric material should possess high thermoelectric figure of merit ( $zT$ ). It is a great challenge for scientists to overcome the obstacles by finding a suitable high-performance material. The goal is to fit three seemingly different properties namely: high electrical conductivity like metals, high Seebeck coefficient like semiconductors and low thermal conductivity like glasses into a single compound to achieve high  $zT$ . Over the last 60 years, scientists have studied several systems, but the most efficient thermoelectric materials consist of hazardous lead (Pb) as major constituent elements which restrict their use for mass market applications. Recently, germanium telluride (GeTe) from the IV-VI metal chalcogenide family recently emerged as a potential candidate for the replacement of Pb-based systems for mid temperature power generation applications. Interestingly, several GeTe-based thermoelectric materials discovered in our lab even outperform the PbTe-based thermoelectrics.

However, the low Seebeck coefficient and high thermal conductivity of GeTe are the two principal constraints in the way of optimizing its thermoelectric figure of merit. Recently, we have reported a high  $zT$  of  $\sim 2.1$  at 723 K in p-type In and Bi co-doped GeTe along with an extremely high TE conversion efficiency of  $\sim 12.3\%$  in a single-leg thermoelectric generator.<sup>1</sup> We have shown that In doping significantly enhances the Seebeck coefficient through the formation of resonance level whereas Bi doping reduces the lattice thermal conductivity due to the formation of extensive solid solution point defects and domain variants.



Although the thermoelectric performance of p-type GeTe has been improved tremendously in recent years, it has been a challenge to find a compatible n-type GeTe counterpart due to the prevalence of intrinsic Ge vacancies. In recent days, we have shown that realization of n-type electronic conduction in GeTe by AgBiSe<sub>2</sub> alloying which lead to evolution in crystal structure and electronic structure. The cubic n-type (GeTe)<sub>100-x</sub>(AgBiSe<sub>2</sub>)<sub>x</sub> ( $x \geq 25$ ) samples have ultralow lattice thermal conductivity ranging from 0.3 – 0.6 W/mK and a maximum zT of ~ 0.6 has been achieved in n-type (GeTe)<sub>50</sub>(AgBiSe<sub>2</sub>)<sub>50</sub> at 500 K. Thus, the development of both n- and p-type GeTe-based thermoelectrics opens new opportunities for mid-temperature range (400-500 K) power generation applications.

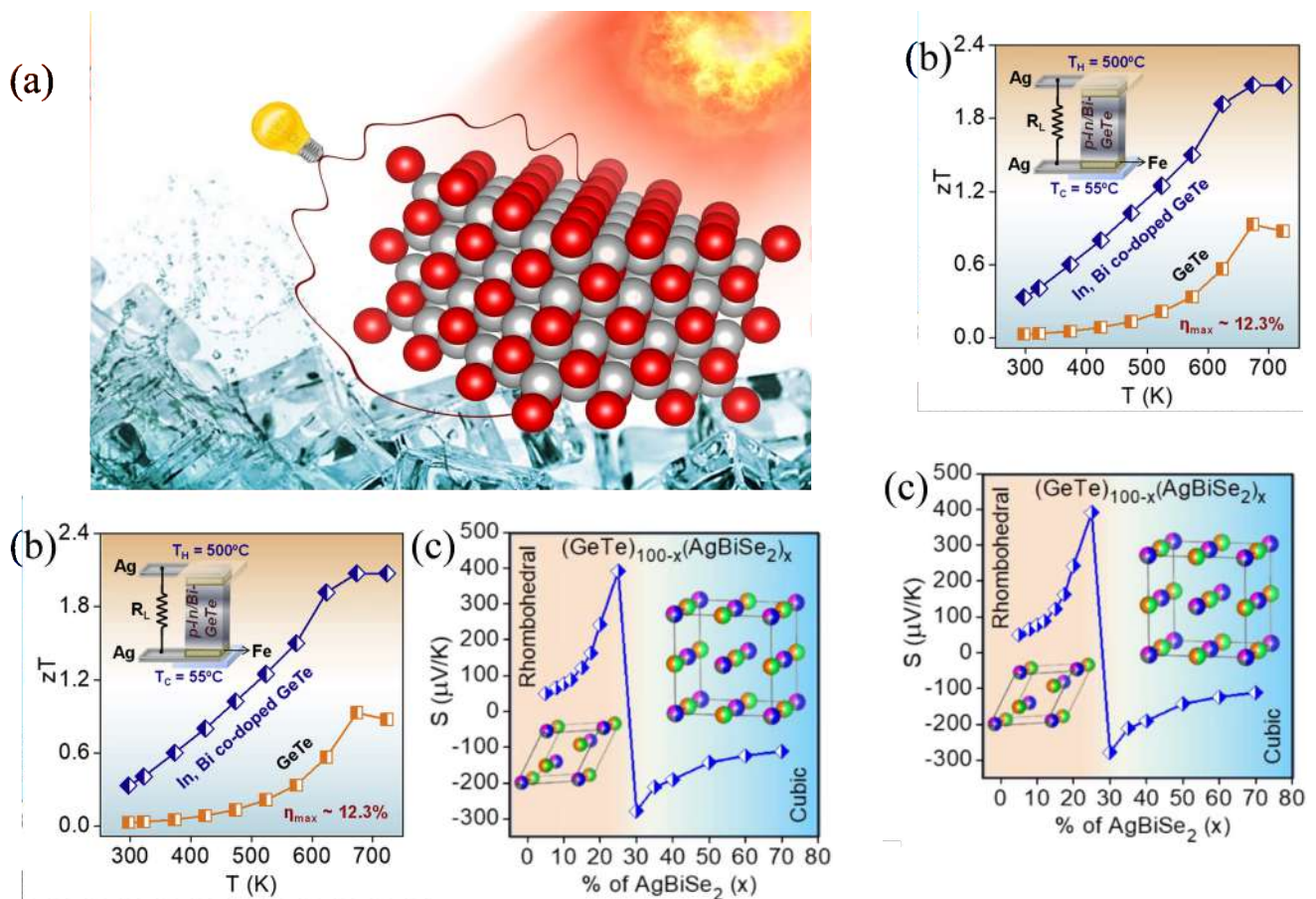


Figure. (a) Schematic of the thermoelectric energy conversion. (b) Thermoelectric figure of merit (zT) of Ge<sub>0.93</sub>Bi<sub>0.06</sub>In<sub>0.01</sub>Te. Inset shows the schematic diagram of the fabricated p-type single-leg device based on this material. (c) Evolution of Seebeck Coefficient (S) of GeTe with increasing AgBiSe<sub>2</sub> concentration in (GeTe)<sub>100-x</sub>(AgBiSe<sub>2</sub>)<sub>x</sub> ( $x = 0 - 50$ ).

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