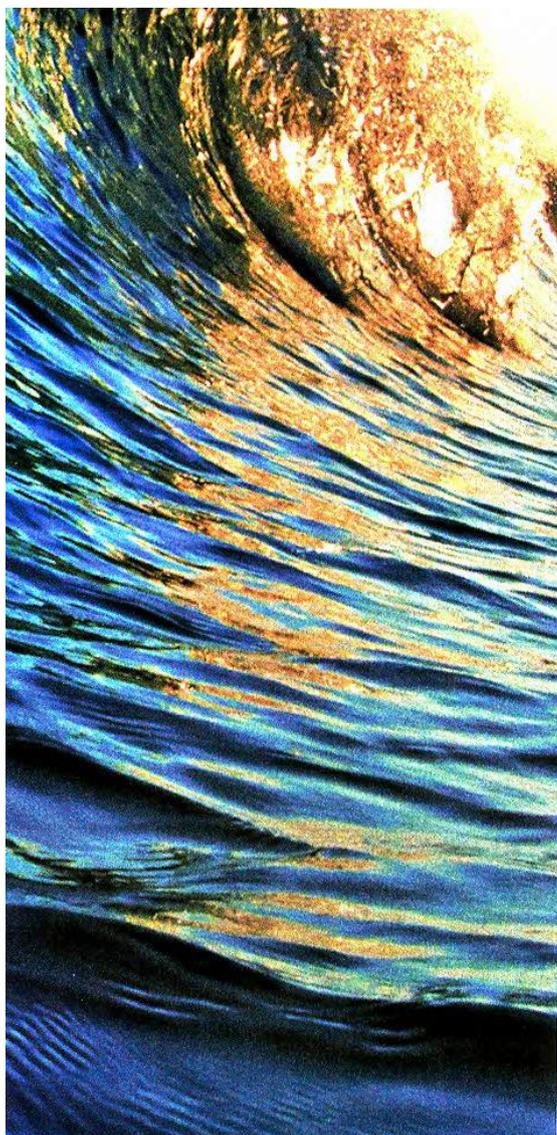


# Batteries and Supercapacitors for Energy Storage and Delivery Needs of India



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## Executive Summary

Batteries are important drivers of modern civilization, powering applications from mobile phones to aircraft and strategic systems. The use of batteries is expected to further grow with the emergence of electric mobility and increased use of hand-held electronic devices. Further, with emphasis on renewable energy, which is intermittent, the demand for batteries from this segment is likely to grow manifold to store and distribute energy and for integrating with existing systems.

Thus, batteries (chemical energy storage) and electrochemical capacitors (electrical energy storage) are considered critical in meeting this requirement, as they are ideally suited to store energy and release it on demand. Their reliability, safety, modularity and affordability make them ideal for applications in sectors such as consumer electronics, telecommunication, medical instrumentation, electric mobility, uninterrupted power supply, electric traction, grid power, defence and space.

It is clear that the sustainability of a society depends on prudent generation and management of electrical energy. With this in mind, the Office of the Principal Scientific Advisor to the Government of India constituted a working group to draw a status report and a roadmap on energy storage technologies for India. This report presents the status of the science and technology of electrochemical energy storage systems as well as Indian expertise, manufacture and market potential, and new directions that need to be pursued for a sustainable energy management. There is a great deal of novel science and research coming from academic and research centers, including on materials and system integration research. However, there is also a growing technology/knowledge gap between the basic science and the battery manufacturing environment that needs to be bridged. To this end, it is mandatory to bring researchers and other experts from academia, government organizations, start-ups and battery manufacturing companies to share knowledge and debate issues and find solutions to technical problems. A mix of academia and industry will open opportunities to move concepts from laboratory to commercialization. The present effort is to bridge the gap between research and production to realize the next big leap in battery power.

This report focuses on both mature and emerging electrochemical energy storage technologies. Technologies under discussion are lead-acid batteries, alkaline batteries (nickel-iron; iron-air; nickel-metal hydride), lithium-based batteries (lithium-ion; lithium-air; lithium-sulfur), redox

flow batteries (vanadium–vanadium; soluble-lead), high-temperature sodium batteries (sodium–sulfur; zebra), and electrochemical capacitors (electrical double layer and pseudo-capacitors; lead–carbon battery-supercapacitor hybrid).

The need for intensive investigations is emphasized by highlighting the fact that current technologies fall short of the performance requirements expected for several existing as well as emerging applications. Given the paucity of our understanding of molecular-level and interfacial processes that are fundamental to the working and failure of these systems, it is necessary that the systems be revisited with the aid of new analytical and characterization tools. Similarly, critical technology gaps must be addressed through new synthetic and processing strategies, engineering design and system modeling, and by pushing materials to their stability limits and tapping into new knowledge on nano- and multi-functional materials. The Indian battery scene and technology readiness levels of battery systems are also briefly discussed. The report culminates by emphasizing the need for establishment of Centers of Excellence in electrochemical energy technology and for putting in place a policy on sustainable energy with stakeholders drawn from the academia, industry and government.

## Preface

Increasing reliance on renewable energy sources, and technological advances in areas such as electric traction, smart grids and portable electronic gadgets have catalyzed renewed interest in energy storage options. The electrochemical mode of energy storage offers flexibility and scalability as well as candidate systems with a range of energy/power densities. With their low costs and low rates of self-discharge, they are particularly suitable for stationary applications as in power grids that are connected to intermittent renewable energy sources such as wind and solar. Batteries are classified by chemistry, and the most common ones are lead-, nickel- and lithium-based systems, which command 48, 10 and 37%, respectively, of the worldwide secondary battery market share. The shares of all the other systems add up to just 5%. Batteries are a fast growing market bolstered by the electronics manufacturing segment as well as by expanding production and use of motor vehicles. The global demand for batteries is forecast to rise by 8.5% per year to \$144 billion in 2016.

Batteries are energy devices. Because energy and power play against each other, increasing one will lead to a loss in the other. This means that if we require high power from a battery, we will extract less total energy than when we require low power. Capacitors, being power devices, complement battery power by allowing very rapid charge and discharge. Accordingly, capacitors will gel well with batteries into the emerging energy-storage landscape. Since the capacitance mode allows storage of electricity directly as electrical charges, electrical-double-layer capacitors can have efficiencies close to 100%. Supercapacitors are a relatively newer technology with a projected global market of \$40 billion by 2020.

In a timely initiative, the Office of the Principal Scientific Advisor to the Government of India constituted a committee of experts in electrochemical energy storage to draw a status report on both mature and emerging electrochemical storage technologies and their suitability in meeting the energy requirements of India in conjunction with energy efficiency, electricity delivery and energy reliability to clearly define future requirements for energy storage from the perspective of applications relevant to transportation as well as electricity distribution and identify critical technology gaps. This report presents the status of the science and technology of electrochemical energy storage systems as well as Indian expertise, manufacture and market potential, and new directions that need to be pursued for a sustainable energy management.

## Abbreviations used in the text

3D	three-dimensional
AC	alternating current
AGM	absorbent glass mat
ARCI	International Advanced Research Centre for Powder Metallurgy and New Materials
CECRI	Central Electrochemical Research Institute
CNT	carbon nanotube
CoE	Center of Excellence
DC	direct current
EDLC	electrical double layer capacitor
EV	electric vehicle
HER	hydrogen evolution reaction
HEV	hybrid electric vehicle
ICEV	internal combustion engine vehicle
IISc	Indian Institute of Science
MH	metal hydride
NMEM	National Electric Mobility Mission
OER	oxygen evolution reaction
ORR	oxygen reduction reaction
PANI	polyaniline
SLI	starting–lighting–ignition
Super NiCad	Super nickel–cadmium battery
TRL	technology readiness level
UPS	uninterrupted power supply
VRLAB	valve-regulated lead-acid (VRLA) batteries
ZEBRA	Zeolite Battery Research Africa

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## 1. Introduction

Batteries are important drivers of modern civilization, powering application from mobile phones to aircraft to strategic systems. Batteries enable us to start our cars, communicate with smart-phones and tablets and power our pacemakers. Batteries are also a key technology for electric-mobility and the new energy economy, suggesting that these chemical energy stores are soon going to be game changers.

With the world electricity consumption expected to grow at 3.6% annually, increasing emphasis is being placed on more efficient technologies with low or zero-carbon footprints for both generation and use of energy. India is embarking on ambitious solar and wind energy projects. The energy from both these sources is, however, intermittent. It is, therefore, necessary to store the energy generated from these sources for continuous supply. Thus, electrical storage technologies are called upon for both storing excess power and for meeting peak-power demands. Indeed, experts consider storage batteries seminal to the success of renewable energy programs.

Uninterrupted power supply (UPS) is another area that begs attention. Power shortage and associated problems such as low frequency, tripping of generators and load shedding are a bane of state electricity boards. Low-cost imports from China and Taiwan as well as high domestic cost of raw materials are major challenges for the manufacturers. The proliferating digital world is a major consumer of UPS batteries.

Electric traction is another area that promises a humongous growth market for batteries. India is also a growing market in this sector. However, battery cost is a hurdle to widespread penetration of electric vehicles. Thus, in order to encourage proliferation of electric vehicles, the Ministry of New and Renewable Energy provides financial incentives: Rs 4,000 for low-speed electric two-wheelers, Rs 5,000 for high-speed electric two-wheelers, Rs 60,000 for seven-seater three-wheelers, and Rs 100,000 for electric cars manufactured in India. Not surprisingly, therefore, several players have entered the fray, some prominent ones being Ampere Vehicles, Hero Ultra, Yo Bikes, ACE Motors, Eko Vehicles, Go Green, Reva, Hero Electric, Mahindra & Mahindra, Mitsubishi, and Tata. Under the National Electric Mobility Mission Plan 2020 (NMEM 2020), 6–7 million electric vehicles are expected to be on the road.

Storage and release of electrical energy is unarguably critical for uninterrupted and non-fluctuating supply with increasing penetration of intermittent renewable power sources. However, only a handful of back-up storage technologies are efficient and at the same time economical. If additional requirements such as sustainability and low-carbon emissions are to be factored in, the choices narrow down to such technologies as pumped-storage hydroelectricity, which, however, comes with the burden of location, environmental conservation and social problems. Other leading energy storage technologies include flywheels, superconducting magnetic energy storage, compressed air energy storage, water electrolysis and methanation, and electrochemical energy storage devices such as batteries and electrochemical capacitors.

Several of these technologies have a fast response time, which is essential if power blackout during peak demand is to be avoided. However, high installation costs and poor efficiency as with water electrolysis and methanation can hamper their widespread use. They must also have low rates of self-discharge. Flywheel and superconducting magnetic energy storage technologies suffer from self-discharge rates of 3–20% per hour and about 12% per day, respectively. By contrast, the self-discharge loss in lead-acid batteries, for example, is only about 5% per month. Batteries and electrochemical capacitors can be cost-effective and allow for flexibility in deployment, which can in turn facilitate widespread use and networking of intermittent renewable energy technologies. Electrochemical storage technologies are also ideal for transportation where instant power should be available for the vehicle for reasonable lengths of time. They are also mature, inexpensive and ensure high levels of safety, reliability and durability. They are ubiquitous, coming in various sizes and capacities, suitable for stationary and portable applications in a broad spectrum of human activity.

It is noteworthy that the dramatic explosion of the portable electronics market owes much to the ubiquitous batteries that power them. However, the days of the conventional battery systems seem numbered. The performance levels of conventional batteries are often found wanting for projected applications, be it in the burgeoning electronics industry or in the transportation sector, where a shift in gears from the internal combustion engine vehicles (ICEVs) to electrically operated vehicles is on the cards. A common sight on the roads at the turn of the century, battery operated cars, which were pushed out of the race by superior

ICEVs, made a transient resurgence in the 1970s as a result of the first oil-shock. However, today, a rebirth of the electric vehicle is both necessary and imminent. Today, we are addicted to oil and seem settled in the cozy comfort of the gas-guzzling ICEVs albeit being confronted by a number of issues such as geo-politics and the consequent oil price wars and disruptions in the supply of petroleum products, the longevity of petroleum resources, and stricter policies on climate change and vehicular emissions. In the battle for alternative fuels for a decarbonized transportation sector, electricity has a definite edge. There is, however, a lingering fear that battery technology has not lived up to the demands of the electric vehicle. Although an immediate choice is the plug-in hybrid electric vehicle, the ultimate goal is an all-electric vehicle. This goal is a major driver in the search for electrochemical storage technologies that are not only radically different from existing ones but also outperform them, for the stakes are too many.

Ranked the tenth largest economy today, India is expected to break into the third position after the US and China. However, its per capita income is not anywhere near those of developed countries. The situation, therefore, demands that high-quality products are made available at low prices. For example, the Government of India's intervention to transform the automotive paradigm from the one based on fossil fuels to electric traction (NMEM 2020) is estimated to cost it Rs 13,000–14,000 crore in the next 5–6 years. While the mission aims to reduce carbon dioxide emissions by 1.3–1.5%, what is overlooked is the fact that bulk of the money that the common man spends on his new electric vehicle will be on the battery pack! There is thus an urgent need to strengthen our base on the expertise and manufacturability of affordable power systems.

This report seeks to discuss all of these issues relating to battery technologies and provides a road map for India.

## **2. Indian scene**

### **2.1. The battery market**

The world demand for primary and secondary batteries is expected to rise by 8.5% per year, accounting for a \$144 billion market in 2016. China will remain the largest and fastest growing market, while the growth of battery market in India will be relatively slower. The growth curve has new contributors other than the portable electronics sector, which includes

grid storage systems based on renewables, electric vehicles, and high-drain electronic gadgets. In the coming years, advanced lead-acid, nickel–metal hydride and lithium-ion batteries are expected to make further forays into specialized applications. Developing nations such as India will register greater market impact due to increasing demands and industrialization. The lead-acid battery market in India is dominated by Exide and Amararaja, which command as much as 70% of the \$4 billion Indian market.

## 2.2. Manufacturing base

India has a world-class manufacturing base for lead-acid batteries. The lead-acid battery market is well established in India. Major players in the organized sector include Amararaja Batteries, Exide Industries, Hyderabad Batteries, NED Energy and Tata Green with the lion's share coming from the first two. There is also a mushrooming unorganized lead-acid battery sector, thriving on borrowed art, catering to a wide section of customers. CECRI has established a national battery testing center, which today caters only to the lead-acid battery industry. The infrastructure, resources, expertise and support base from allied industries can come in handy for launching new related systems such as the lead-carbon hybrid battery and the soluble lead redox flow battery. The many now-defunct nickel–cadmium battery units can easily be transformed into manufacturing units for the nickel–iron, iron–air and nickel–metal hydride batteries. This sharply contrasts with the nearly non-existent infrastructure available for lithium-ion battery manufacture.

In January 2013, India had 862.62 million mobile phone subscribers, which is just one application area for lithium-ion batteries. Surprisingly, for a country that boasts of 862.6 million mobile subscribers, India does not have even a single manufacturing base for lithium-ion batteries. It must be noted in passing that Future Hitech Batteries Limited, which is a rebirth of the Twenty First Century Battery Limited, has inherited an obsolete technology from Bellcore. Indocel Technologies is one company that imports cells from their principals, assembles batteries of required specifications complete with battery management systems, and supplies to targeted customers. Apart from the high initial investments, especially in specialized facilities such as dry rooms, the challenges in adopting new methodologies relating to rapidly-emerging battery chemistries also pose a problem to potential investors. Bereft of a conducive manufacturing platform, India is ill-prepared to push forward with

establishment of this battery technology. It is time policy makers identified core challenges related to lithium battery manufacturing.

### **3. Electrochemical energy storage systems**

There are two types of electrochemical energy storage systems: (i) batteries that store energy as chemical energy in their active materials (chemical storage), and (ii) electrochemical capacitors that store energy as charge (capacitive storage). Currently available electrochemical storage technologies fall short of projected day-to-day requirements, as for example for electric vehicles, in terms of their energy and power densities, and even in terms of the time they take to get recharged. Our understanding of the fundamental and inter-related processes that govern their operation, performance, safety limits and failure remains alarmingly poor even after two hundred years of the demonstration of the first galvanic cell by Alessandro Volta. Much needs to be researched before we can translate our understanding of the fundamental molecular processes into practical devices.

In this report, we review the current status of electrochemical energy storage technologies and their limitations, and address key directions and new materials that can lead to high-performance energy storage devices. The individual systems chosen for discussion are considered mature and emerging, suitable for a sustainable future, and adequate enough to meet the needs of the Indian populace.

### **4. Battery systems**

#### **4.1. Lead-acid batteries**

A mature technology, the lead-acid battery is backed by 150 years of development. With less than \$150/kWh, lead-acid batteries are unrivalled in terms of cost-effectiveness. Today, lead-acid batteries command more than half of a whopping \$60 billion world battery market, with India's share of the market being about \$4 billion, out of which the share for automotive batteries is Rs 10,000 crore while that for industrial batteries is Rs 10,000 crore. The lead-acid market is projected to grow by 5–20% in various application sectors in the coming years. Lead-acid batteries are commonly used for starting-lighting-ignition (SLI), deep cycling and stand-by applications.

The battery operates on the double-sulfate reaction in which both the active materials, spongy lead in the negative plate and lead oxide in the positive plate, are reversibly converted into lead sulfate. During discharge, lead dioxide and lead react with sulfuric acid to form a non-conducting solid product of lead sulfate. Both the discharge reactions are accompanied by an increase in the volume of the solid phases: the volume increase for the transformation of  $PbO_2$  to  $PbSO_4$  is 92%, while that for  $Pb$  to  $PbSO_4$  is 164%.

There are three types of lead-acid batteries in common use: (a) batteries with flooded electrolyte, (b) flooded-electrolyte low-maintenance lead-acid batteries with a large excess of electrolyte, and (c) batteries with immobilized electrolyte and a pressure-sensitive (safety) valve, usually referred to as valve-regulated lead-acid (VRLA) batteries. Normal flooded-electrolyte batteries use lead-antimony alloy positive grids. Their water consumption, which is low in the initial stages, increases as much as five times toward the end of their lives. The low-maintenance-type flooded-electrolyte batteries use low antimony alloy positive grids. Such batteries with calcium alloy grids consume only about one-tenth the water needed by equivalent sized antimony cells. In these batteries, the water requirement is low and constant throughout their lives. VRLA batteries, based on the oxygen recombination cycle, do not vent gases and do not require periodic topping. Moreover, these batteries offer freedom of battery placement, increased safety, and superior performance. Their cycle life and deep discharge capability depend on the type of construction. In flooded-electrolyte lead-acid batteries, the electrolyte is filled to a level above the top of the plates and bus bars. This has the disadvantage that the cells have to be vented to release the gases liberated during charging, namely, oxygen at the positive plate and hydrogen at the negative. The consequence of this venting is that the batteries have to be used only in the upright position; otherwise leakage of electrolyte takes place. Also, the released gases carry a very fine mist of acid, which is highly corrosive. The seepage of acid on the top cover of the battery leads to a leakage current, resulting in increased self-discharge and ground-shunting. The latter is a process by which the battery drains itself by grounding or by discharging through a grounded body, as for example of an electric car. The flooded-electrolyte lead-acid battery requires checking of specific gravity of the electrolyte, periodic addition of water to maintain electrolyte level above the top of the plates, and recharge soon after the battery discharge to mitigate hard sulfation that causes loss in battery capacity. On the other hand, VRLA

batteries, based on the oxygen recombination cycle, do not vent gases and do not require periodic topping. Moreover, these batteries offer freedom of battery placement, increased safety, and superior performance. Valve-regulated versions of the lead-acid battery are sensitive to temperature and cyclic applications.

Commercially available lead-acid batteries have specific energies of 25–40 Wh/kg (60–75 Wh/l). Their discharge-charge watt-hour efficiencies lie between 80 and 85%. Despite the fact that their current energy densities are rather low and their cyclability only of the order of a few hundreds of cycles, they remain the preferred workhorse for a variety of applications where weight and volume are secondary. The flooded-electrolyte lead-acid batteries are the traditional types used in stationary applications although the VRLABs are now increasingly being used. The latter use an absorbent glass mat (AGM) or a gelled mass as the electrolyte and have a compacted stack construction. Continual improvements in design and use of alloying additives have resulted in VRLABs with a higher shelf-life and cycle-life.

Contrary to popular belief, scientists have come to recognize that there is more to be expected from lead-acid batteries. In fact, until not long ago, they were stereotyped with the common SLI batteries, whose performance expectations are limited. The entry of high-energy batteries such as nickel–metal hydride and lithium-ion batteries triggered research on tapping deeper into the performance capabilities of lead-acid batteries. Electrode reactions in lead-acid batteries give rise to several products with differing morphologies. Deep-discharges, as expected in applications such as electric vehicles, would mean maximizing volume and morphological changes in the active materials, a consequence of which is shedding of the active mass. Deep-discharge and failure to routinely return to full state-of-charge lead to sulfation of the negative plate. Abusive overcharge also leads to corrosion of the positive plate. In stationary applications such as power grids and roof-top photovoltaic installations, erratic regimes may be expected.

In recent years, the science and technology of lead-acid batteries has seen a paradigm change, opening up possibilities in higher-energy-density applications. For example, both mechanical properties and corrosion resistance of lead grids have been improved by the use of alloying additives. A debilitating phenomenon in lead-acid batteries is sulfation, which is now sought to be mitigated by use of a thin layer of carbon in the negative plate. In fact, the results have been so dramatic that Honda replaced the nickel–metal hydride batteries in its

Insight HEVs with these batteries. Other recent developments include 3D polysiloxane-based gel electrolytes as well as separators and light-weight-current collectors. To retain the market position, to withstand the persistent tough competition from other technologies, several innovations have been made in the technology of lead-acid batteries that include (a) lead-carbon ultrabatteries, (b) bipolar lead-acid batteries, (c) soluble-lead redox flow batteries, (d) substrate-integrated lead-carbon supercapacitors, (e) thin-plate pure-lead lead-acid batteries, (f) tri-polar lead-acid batteries, (g) strap-grid tubular positive lead-acid batteries, (h) carbon composite foam current collector lead-acid batteries, (i) reticulated vitreous carbon current collector lead-acid batteries, (j) lead-infiltrated ceramic bipolar-plate lead-acid batteries, and (k) synthetic-fiber-reinforced AGM lead-acid batteries.

An Indian lead-acid battery industry has acquired know-how on carbon composite foam current collector lead-acid batteries from Firefly Energy in the US. Atraverda is developing

Table 1. Performance benefits against improvements in lead-acid battery technology.

<b>Technology</b>	<b>Performance benefits</b>
Bipolar	Dramatic reduction in the number of battery components; low volume and weight; higher energy and power densities; low mass of lead per kWh.
Tripolar	Good high temperature performance; good rate capability.
Substrate-integrated lead-carbon	High power density; supports partial SOC operation; good high rate charge.
Strapgrid tubular	Improved power output; good charge acceptance; best suited for VRLA with AGM separator.
Carbon foam current collector	High energy and power densities; good cycle life; composite plate material is lighter, longer-lasting, with high active material utilization; foam negative plates give performance comparable to Ni-MH, but at lower manufacturing costs.
RVC current collector	High energy and power densities; good cycle life and high-rate performance.
Lead-infiltrated ceramic bipolar plate	High energy and power densities; good cycle life and high-rate performance.
Thin plate pure lead	Good rate capability.
Synthetic fiber reinforced AGM	Good tensile strength and puncture-resistance; minimal short circuit during assembly; good resistance to oxidation especially at elevated temperatures; improved battery life.
Enhanced flooded lead acid battery	Good deep discharge cycle
Lead-carbon ultrabattery	High power density; long cycle life; supports partial SOC operation; good high rate charge acceptance; good low temperature cranking.
Soluble redox flow battery	Employs a single electrolyte; operates without separator.

new bipolar lead-acid batteries for the Indian market that will be smaller, lighter and more environmentally-friendly. Raman FibreScience in Mysore has initiated manufacturing of synthetic fiber-reinforced separators for lead-acid batteries. In brief, the Indian lead-acid battery is trying to adopt the state-of-the-art technology.

Lead-acid batteries operate over a wide temperature range, between  $-20^{\circ}\text{C}$  to  $+50^{\circ}\text{C}$ . Lead is toxic, but lead-acid batteries can be recycled with 99% recovery of lead. Two key issues that have restricted wider commercial adaptability of lead-acid batteries are their low cycle-life and limited specific energy. Performance benefits accrued by adoption of improvements in the lead-acid battery technology are presented in Table 1.

#### 4.2. Alkaline batteries

Alkaline batteries based invariably on the nickel oxyhydroxide cathode are superior to the lead-acid battery in terms of energy turnover, ability to deliver continuous power, fast recharge capability and long service-life. The nickel-iron battery was extensively deployed in the railway carriages of the erstwhile Soviet Union. The instability of the iron electrode in alkaline medium put the lid on the nickel-iron battery technology. The most popular among alkaline batteries is the nickel-cadmium system, which dominated the market for several decades. SAFT Batteries have commissioned the world's biggest nickel-cadmium battery bank (40 MW; 13,760 cells) for stationary applications in Alaska. An undesirable characteristic of nickel-cadmium batteries, especially those with sintered-type cadmium electrodes, is memory effect. Furthermore, their ability to recharge is limited by their substantial negative temperature-coefficient. Their self-discharge rates are also high. These, together with the toxicity of cadmium, have led to a waning in the production of nickel-cadmium batteries worldwide. By contrast, nickel-metal hydride batteries have shown promise in hybrid electric vehicles albeit being expensive and prone to heavy self-discharge. At present, the Indian market share for nickel-based batteries stands at about US \$ 30 million.

##### *4.2.1. Nickel-iron battery*

In hibernation for decades, the nickel-iron system has begun to catch the attention of policy makers. The resurrection of the system rests heavily on its techno-economic feasibility for a number of applications arising out of recent technological developments. Two problem areas

that are being addressed are: (i) catalytic recombination of hydrogen and oxygen gases that are evolved in the battery, with possibilities of a sealed battery, and (ii) electrolyte/electrode additives that can shift the overvoltage for the hydrogen evolution reaction (HER). Latching on to the new developments should propel nickel–iron battery for applications wherefrom lead-acid and nickel–cadmium batteries have been withdrawn. Its cost competitiveness is obvious considering its longevity, typically 3,000 cycles, corresponding to a calendar life of about 20 years. Particular areas of application should include stationary ones as in photovoltaic installations, where its mechanical robustness and long life even under adverse operational conditions such as over-charge, over-discharge, charge-stand, discharge-stand and inadequate maintenance would be very attractive.

The discharge reactions of the iron electrode proceed in two steps, yielding  $\text{Fe(OH)}_2$  in the first discharge step and  $\text{FeOOH}$  in the second. The open-circuit potential of the charged alkaline iron electrode is always cathodic to the potential for HER in the same solution, which renders the metal thermodynamically unstable. But the extraordinary robustness and service life are appealing for civilian applications. The nickel cathode is a well-established system. Under shallow discharge regimes, the nickel electrode is known to sustain more than 20,000 cycles as in Super NiCad batteries for space applications. The degree of utilization of the nickel electrode varies from about 60% for pocket plate or pressed plate electrodes to more than 90% for sintered plate electrodes. Freshly charged nickel electrodes lose 0.1–0.2% capacity a day by self-discharge at 25°C, which may be reduced with additives such as CdO. Cycling the iron electrode is fraught with problems of poor charging efficiency (50–70%) and low electrode utilization. Therefore, to offset the loss and to achieve satisfactory performance, iron electrodes are typically overcharged by 60–100%.

Under the tropical conditions prevailing in India, where ambient temperatures can cross even over 45°C, it is preferable to use an electrolyte composition of 18% NaOH and 0.8–1.0% LiOH (instead of the commonly employed 25% KOH + 1.0–1.2% LiOH). The less expensive NaOH-based electrolyte sustains a larger number of cycles under high ambient temperatures prevailing in India although that advantage comes with a small penalty in terms of a slightly reduced nominal capacity. NaOH has a lower molecular weight than KOH and is also used at a lower concentration, which give an additional advantage of a lowered battery-weight.

Recently, the beneficial effect of sulfide additives on the cyclability of the iron electrodes has been demonstrated, with a utilization efficiency of 68% of the rated capacity at 1C rate. However, full exploitation of the system rests on control of the wasteful evolution of hydrogen during charging. It was also shown that *in situ* electro-deposited bismuth led to substantial inhibition of the kinetics of HER. The hydrogen evolution that occurs during charging lowers the round-trip energy efficiency and necessitates constant maintenance to replenish lost water. The gas evolution would mean that the battery cannot be sealed. Carbonation of the electrolyte is thus a serious concern. It is clear, therefore, that suppression of the evolution of hydrogen and sealability of the nickel–iron system have far-reaching ramifications not only in raising the overall energy efficiency and lowering the cost, but also in facilitating its penetration in various spheres of application. Recently, a nickel–iron cell with a recombination catalyst was reported that paves the way for the development of a sealed version of the battery.

Another concern with these batteries is their poor high-rate discharge performance. Several applications such as electric vehicles and grid-scale energy storage demand battery discharge at C or C/2 rates. It is found that a combination of high-purity  $\alpha$ -iron incorporated with bismuth by electro-reduction of bismuth sulphide exhibits a ten-fold decrease in hydrogen evolution rate without interfering with the kinetics of the iron electrode reactions. It is reported that an unprecedented 96% charging efficiency at a specific capacity of 400 mAh/g for the iron electrode and a twenty-fold increase in capacity at C/2 rate is now achievable. These breakthroughs in the technology of the alkaline iron electrode should augur well for large-scale exploitation.

Scientists at Stanford University constructed a nickel–iron battery with iron oxide grown on graphene as the anode and nickel hydroxide deposited on multi-walled carbon nanotubes as the cathode. The nano-configuration displayed a dramatic improvement in performance: it could be fully charged in about two minutes and discharged in less than 30 seconds. This is a jump of more than 1,000 times over the conventional rates of charging and discharging. The new nanomaterial-based technology opens up opportunities especially in electric traction. Because the battery allows fast charging and discharging, one would be tempted to put it to more frequent use, like a supercapacitor.

In recent years, interest in nickel–iron batteries is being revived since these batteries are reliable and inexpensive, can be subjected to high discharge rates, exhibit good low- and high-temperature behavior with long cycle life, can undergo two-step charge-discharge, can provide reserve charge during the second step of discharge, are electrically and mechanically rugged, and, above all, are environment-friendly. Today, it looks even feasible to assemble nickel–iron batteries in sealed form by incorporating a gas-recombination catalyst. Its suitability for India is also emphasized by the better performance of the system with inexpensive NaOH-based electrolytes under high ambient temperatures. In fact, the economics, eco-friendliness, longevity and performance of these systems are too favourable to be dismissed under the euphoria of new inventions. It is high time that the Government of India encouraged developmental efforts in these systems for public good.

#### *4.2.2. Iron–air battery*

Arguably, no battery can surpass the iron–air battery in terms of cost-competitiveness. The battery has an additional advantage, characteristic of metal–air batteries, which is that the cathode-active material (oxygen) need not be contained in the battery. Like the nickel–iron battery, the iron–air battery also gives a two-plateau discharge curve. Although the open-circuit voltage of the iron–air cell is 1.28 V, its working voltage is only 0.7–0.8 V.

The iron–air battery, first explored as a concept 40 years ago, is being revamped as an inexpensive, rechargeable, high energy density power source. Once a prime candidate for traction and military applications, they are now projected for large-scale energy storage and as a candidate system that can accelerate the adoption of renewable energy sources. The theoretical specific energy density of the iron–air battery is 955 Wh/kg, which is about three times that of the nickel–iron battery and four times that of the lead-acid battery. The iron–air system comes in two versions: electrically rechargeable and mechanically rechargeable. The former has a lower specific energy than the latter, but the lower specific energy is somewhat offset by the advantage of a lower life-cycle cost. The electrically rechargeable version may have a bi-functional cathode or an auxiliary (third) electrode, which is used only for recharging the battery. The alkaline iron anode does not suffer non-uniform and dendritic metal deposition and shape change upon recharge.

A notable disadvantage of metal–air batteries, however, is their poor energy efficiency (around 50%). The realization of such batteries rests heavily on the development of a bi-functional oxygen electrode and oxygen-selective membranes for mitigating carbonation of the electrolyte. Besides their low cost, their environment–friendliness is a rallying point for developmental activities in metal–air systems. It is now firmly believed that the future is in the air.

The low solubility of oxygen in the electrolyte and the need to electrocatalyze the reduction of oxygen at the three-phase zone (liquid–gas–solid interface) of the cathode present unique problems especially on oxygen transport properties in the electrolyte. Thus, the success of the electrically rechargeable iron–air battery rests solely on the perfection of the air-breathing cathode. This means that electrochemical problems of intrinsically slow reactions, high overpotentials and the poor reversibility of oxygen electrochemistry must also be overcome. This requires the catalytic bi-functional air electrode to support both ORR (oxygen reduction reaction) and OER (oxygen evolution reaction). Alkaline electrolytes have a disadvantage that they absorb carbon dioxide in the air to form carbonates. The low solubility of carbonates in alkaline media results in clogging of the pores of the air-breathing cathode. It is thus necessary to feed purified air or use a membrane that is selectively permeable to oxygen. A circulating electrolyte design may also be employed as saturation by carbonate is attained much more slowly than with an immobilized electrolyte design.

ORR in alkaline solutions is favoured by fast kinetics and low overpotentials. On metal surfaces, it can proceed via a four-electron or a two-electron pathway. While the four-electron pathway generates  $\text{OH}^-$  ions, the two-electron pathway leads to the formation of peroxide ions. Direct transformation of oxygen to  $\text{OH}^-$  ions by the four-electron pathway is desirable due to its high energy efficiency. The peroxide species produced by the two-electron pathway is corrosive and can lead to premature degradation of the cell.

Satisfactory rechargeability of the iron–air battery depends not only on the electrocatalysis of the normally slow ORR during battery discharge, but also on accelerating the OER during battery charging. It must be noted that for an efficient bi-functional air electrode, the overpotentials for both ORR and OER should be minimal in order to maximize power output and round-trip efficiency. Noble metals can electrocatalyze both ORR and OER, although their ability to sustain extended cycling is yet to be established. It is noteworthy that for

widespread use of iron–air batteries, the technology should be based on cheap non-noble metal catalysts only. Carbonaceous materials are among such inexpensive alternatives. Vertically aligned nitrogen-doped carbon nanotubes have been shown not only to catalyze the four-electron ORR, but also outperform Pt/C catalysts for ORR activity and durability. Another class of non-noble ORR catalysts can be found in oxides, chalcogenides, nitrides and carbides of transition metals. Manganese-based spinels and perovskites, in particular, exhibit high activity and durability in alkaline electrolytes, and are among prime candidates as catalysts for both ORR and OER. Other promising oxides include nanocrystalline  $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$  spinels,  $\text{Co}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4$ –N-doped reduced graphene oxide. Fundamental aspects of electrocatalysis must be also revisited especially in the light of advancements in materials electrochemistry. Modeling and computational quantum chemistry may lend a helping hand in the design of such materials.

New avenues for exploitation lie in designing high-surface area nanostructured catalytic surfaces and mimicking oxygen chemistries in Nature. Inspired by a cubane-like  $\text{CaMn}_4\text{O}_x$  active site, the biological catalyst found in the oxygen-evolving center in photosystem II, a nanostructured  $\text{Mn}_3\text{O}_4$  catalyst has been designed that exhibits ORR and OER properties comparable to those of precious metal catalysts. Enzymes with redox-active sites capable of supporting both ORR and OER could also be a biological answer to the bi-functional electrode. In contrast to the rigid surfaces provided by inorganic solid catalysts, enzymes present flexibility in redox sites and geometry. Nature can also be relied upon for designing the air-breathing electrode. For example, respiratory organs such as human lungs and fish's gills allow efficient intake of oxygen at interfaces involving the solid, liquid and gas phases.

#### *4.2.3. Nickel–metal hydride battery*

Cadmium being toxic, alternatives to the nickel–cadmium system began to be explored, which resulted in the nickel–metal hydride system. The nickel–metal hydride battery uses alloys of  $\text{AB}_2$  (A: drawn from Ti, V, Zr, etc.; B: Ni, Co, Cr, Mn, Al, Sn, etc.) and  $\text{AB}_5$  (A: La, Ce, Pr, Nd, or misch metal; B: Ni, Co, Mn, Al, etc.) compositions as the anode. Improvements in the technology include use of a new  $\text{A}_2\text{B}_7$  composition and PEO-KOH gelled electrolyte that ensure 80% coulombic efficiency. The cell reactions involve a cyclic transfer of protons between the metal hydride (MH) anode and the  $\text{NiOOH}$  cathode.

Although nickel–metal hydride batteries have been popular power sources for consumer electronics and electric traction, it is only recently that they began to be considered for UPS and telecommunication. A major disadvantage of nickel–metal hydride batteries is their high rates of self-discharge (typically 30% per month). Moreover, its discharge-charge watt-hour efficiency is only about 80%. Both nickel–metal hydride and nickel–cadmium systems have similar cell voltages, but the former is free from memory effect. They have moderately high specific energies and tolerate temperatures up to 70°C, a trait that not many other systems can boast of. Despite its superior performance characteristics over the nickel–cadmium system, nickel–metal hydride batteries are up against lithium-ion batteries in competing for a share of the market.

Vehicular traction is one single application area where alkaline batteries hold promise due to high power capability and long endurance both in terms of cyclability and service life. For example, these batteries have been demonstrated to endure 10 years service in automobiles and more than 200,000 running km. Developments in this direction include replacement of the sintered nickel electrode with a foam electrode, bringing about 50% improvement in volumetric capacity. Recent resort to highly porous foam electrodes and new varieties of high-density nickel hydroxides has helped raise the volumetric charge density from 450 Ah/l for the sintered electrode to 700 Ah/l for the foam electrode. Similarly, a 30% increase in volumetric charge density has been achieved by simple replacement of the sintered cadmium electrode with a cadmium slurry electrode. Other developments include use of thin separators, new electrode designs and electrolyte compositions, all of which have brought about substantial improvements in the performance of the battery.

Today, the use of nickel–cadmium batteries is limited to special applications where nickel–metal hydride batteries would be found unsuitable. India is blessed with huge deposits of rare earth elements all along its southern coastal belt. Therefore, cost considerations that have put a brake on its widespread use elsewhere may not be much of a constraint for India. This sharply contrasts with the scenario for lithium-ion technologies that depend entirely on imports for lithium metal and lithium chemicals. The metal components must be recycled for sustaining this metal-rich technology as recovery procedures for nickel from spent batteries are already established, although rarely practised. Lead times for manufacture can be shortened by re-activating defunct nickel–cadmium plants.

### 4.3. Lithium-based batteries

Lithium-ion batteries in commerce contain a variety of cathode materials such as layered lithiated transition metal oxides, lithium-manganese spinel oxide and lithium iron phosphate, although the anode-active material is usually graphite. These batteries represent the cutting edge of electrochemical science and technology today. Bestowed with energy densities of 150–200 Wh/kg, low self-discharge rates and nearly 100% discharge-charge efficiency, they have already captured a sizeable and niche market in portable gadgets. Although considered very expensive for applications such as transportation and grid storage, they are expected to vie for these markets once their costs are brought down by mass production. A major portion of the cost arises from specialized processing and assembly lines as well as from the adoption of safety measures. As for environmental impact, technologies are available for recovering transition metals such as cobalt from spent batteries. Lithium oxides and lithium salts can also be recycled although their content in lithium-ion batteries is below 1% by weight. Nevertheless, given that India is not blessed with major reserves of lithium, recycling the metal from spent batteries should be a priority in the long run.

Current technologies aim at replacing the toxic and expensive cobalt in the electrodes with low-cost and eco-friendly metals such as iron, manganese, titanium, etc. Low-cobalt alternatives include  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  and  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ , spinel electrode materials such as the high-voltage  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , and olivines such as  $\text{LiFePO}_4$  and  $\text{LiFe}_{0.8}\text{Mn}_{0.2}\text{PO}_4$ . A major breakthrough was made by the introduction of  $\text{LiFePO}_4$  as a cathode and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as an anode. Systems based on the above two materials have lower voltages, which render them safer. On the anode side, much headway has been made in realizing practical specific capacities much above that of the conventional graphite. The new anode-active materials include alloy anodes, conversion electrodes and silicon. Replacement of the carbon anode with high-capacity silicon, especially in nanowire form, is attracting much attention. More stable and non-flammable electrolytes, including ionic liquid-based ones, are being investigated upon. Lithium-ion batteries have now become commonplace and are the choice systems for grid storage, electric vehicles, telecommunication and photovoltaic applications.

The basic reactions in lithium-ion batteries may be explained taking the carbon-lithium cobalt oxide couple as an example. Cells are assembled in the discharged state, which means that they must be charged before use. New chemistries based on lithium are emerging, which

include the lithium–sulfur and lithium–air systems. A practical energy density of 350 Wh/kg has already been demonstrated for the lithium–sulfur system. The lithium–sulfur system could potentially double the specific energy of lithium-ion batteries and offer competitive cost. Much ground needs to be covered before problems associated with cyclability of the positive and negative electrodes are solved. Safer and long-lasting solid electrolytes are also being investigated. If integrated in a lithium–air battery, they should give a practical energy density of 1,700 Wh/kg. The importance of this system should be viewed from its theoretical energy density of 13,516 Wh/kg, which surpasses the theoretical value of 13,343 Wh/kg for gasoline. The realization of a practical lithium–air battery is even more formidable. There are a multitude of technical challenges to its realization including cyclability of the lithium anode, bi-functional electrodes for the rechargeable cathode, charge-discharge rate capability of the cathode, identifying electrolyte compositions, and designing membranes permeable to the electrolyte but impermeable to water and carbon dioxide.

Safety has been a recurring theme in lithium-ion batteries. The several recalls of products, especially by manufacturers of laptops and automobiles, and more recently, the grounding of Boeing's Dreamliner fleet, have not helped penetration of this technology into large-scale applications. While lithium-ion batteries come with built-in safety methodologies based on shutdown separators and electrical/pressure interrupts (limited to 18650 cells), manufacturers fall back mainly on the expensive and more reliable safety circuitry for ensuring safety of the batteries. A complicating factor is the absence of uniform, standardized regulations for large batteries. This arises from the very nature of lithium-ion battery technologies that rely on a variety of active materials for their electrodes and even on a variety of electrolyte formulations.

Safety concerns arise not only from the fact that lithium-ion batteries have highly oxidizing and reducing materials but also because their designs have an inherent drawback of poor heat dissipation. Furthermore, the potential ranges experienced in these cells are beyond the thermodynamic stability windows of the electrolytes. The temperature of a cell is determined by the heat balance between the amount of heat generated and that dissipated by the cell. Above a certain temperature (130–150°C), exothermic chemical reactions between the electrodes and electrolyte begin, raising the internal temperature of the cell. If the heat is not dissipated, the cell temperature will rise abnormally, accelerating the chemical reactions,

and eventually leading to thermal runaway. Possible exothermic reactions that trigger thermal runaway are: (i) thermal decomposition of the electrolyte; (ii) reduction of the electrolyte by the anode; (iii) oxidation of the electrolyte by the cathode; (iv) thermal decomposition of the anode and cathode; and (v) melting of the separator and the consequent internal short. Lithium-ion batteries are designed for applications where size and weight are a premium and, therefore, a lower thermal capacity is an unavoidable penalty. Thus, heat dissipation in lithium-ion batteries turns out to be a major engineering challenge, especially for those designed for high power applications.

#### 4.4. Redox flow batteries

Redox flow batteries consist of two electrolytes each with a redox couple. The solutions, stored in separate tanks, are pumped through a cell in which chemical energy associated with the redox couples is converted to electrical energy. The most common of these redox couples are based on vanadium–vanadium, vanadium–bromine, sulphur–bromine, zinc–bromine, cerium–zinc, iron–chromium, and lead–lead. They have energy densities of about 35–50 Wh/kg only. However, they have a long operational life of about 40 years or tens of thousands of discharge cycles. Their energy and power can be increased independently of each other: energy by increasing the size of the electrolyte tank and power by increasing the size of the cell. Several commercial plants are in operation for grid storage. Because flow cells operate for decades on end and generate hardly any waste product, their environmental impact is zero except probably during installation and dismantling. The vanadium–vanadium redox flow battery (with  $V^{5+}/V^{4+}$  and  $V^{3+}/V^{2+}$  redox couples), the iron–chromium flow battery (with  $Cr^{3+}/Cr^{2+}$  and  $Fe^{3+}/Fe^{2+}$  redox couples) and the soluble lead redox flow battery are among candidate systems that must be pursued.

##### *4.4.1. The vanadium–vanadium redox flow battery*

One of the most popular redox flow batteries is the vanadium redox flow battery, which exploits the ability of vanadium to exist in four oxidation states in solution. An added advantage of this property is that there is only one active element in both anolyte and catholyte, which greatly reduces chances of cross-contamination of the anolyte and catholyte. The vanadium–vanadium redox flow battery is an excellent candidate for large-scale

stationary storage. It consists of an assembly of power cells that contain an active electrolyte of vanadium in dilute sulphuric acid. An ion-permeable membrane separates the two half-cells. Electrochemical reactions take place on inert carbon felt electrodes from which the current is collected. The rest of the battery assembly consists of mechanical components such as pipes, pumps and flow tanks. The electrolyte has an indefinite life and is reusable.

#### *4.4.2. Soluble-lead redox flow battery*

One of the offshoots of the science and technology of lead-acid batteries is the soluble lead redox flow battery, a system that offers potential cost and lifetime advantages. In this system, the active lead is present as a single electrolyte, which eliminates the need for separator or membrane, simplifying the cell design and reducing cost. A further reduction in cost and battery weight is achieved by use of carbon-based electrodes instead of lead-based ones. In addition, the improved resistance to sulfation and corrosion of carbon-based electrodes can lead to extended cycle life.

The battery is based on the electrode reactions of lead(II) in methanesulfonic acid. During cell charging, the soluble lead species are converted into a solid phase, with the reverse reactions occurring during discharge. The lead redox flow battery differs from the lead-acid battery both in concept and potential market. It is easy to see that the former represents a quantum jump from the small box-type lead-acid batteries, catering particularly to large-scale storage applications. At the laboratory scale, the lead redox flow battery exhibits a coulombic efficiency of >85% and an energy efficiency of ~65%.

A critical issue in the long-term operation of this system is the chemical balance, which must be restored on completion of a full charge/discharge cycle. However, restoration of the electrodes and the electrolyte in their original states after repeated cycling can happen only if the current efficiencies for the deposition/dissolution of lead and lead dioxide are the same. This means that there should be little gas evolution and current efficiencies at the two electrodes should be close to 100%. A few other challenges also remain to be tackled before this system can be made practical. One of them is the crystalline form in which lead dioxide is deposited upon recharge. Lead dioxide is known to occur in two polymorphs:  $\alpha$ -PbO<sub>2</sub> (orthorhombic) and  $\beta$ -PbO<sub>2</sub> (tetragonal). Because the two phases have different physical properties, control of the structure of the deposited PbO<sub>2</sub> is crucial to the performance and

lifetime of the flow cell. Furthermore, the reversibility of the deposited  $\text{PbO}_2$  material is a major performance-limiting factor. With increased cycle number, the amount of  $\text{PbO}_2$  that remains on the cathode also increases, depleting the electrolyte of  $\text{Pb}^{2+}$  ions available for subsequent charging of the cell. Over time, the energy storage capacity of the cell gets diminished. On the anode side, lead can deposit as dendrites capable of shorting a cell in bipolar stack architecture.

The formation of dendritic lead,  $\text{PbO}_2$  creep and  $\text{PbO}_2$  sledging have been identified as possible failure modes, all resulting in electrical shorting between the positive and negative electrodes. Growth of dendritic lead is observed under high current charging and discharging.  $\text{PbO}_2$  creep can eventually bridge inter-electrode gaps.  $\text{PbO}_2$  sludges can build up in areas of low electrolyte flow and through sedimentation onto horizontal cell components such as electrode spacers and inlet manifolds.

#### 4.5. Sodium–sulfur and zebra batteries

The key to success of the molten sodium-based batteries is a solid membrane of  $\beta\text{-Al}_2\text{O}_3$  (often doped with  $\text{Li}^+$  or  $\text{Mg}^{2+}$ ) with excellent sodium ion conductivity at elevated temperatures. Operating at 300–350°C, the sodium–sulfur battery gives an energy density of 140–170 Wh/kg at an average voltage of 1.78–2.08 V. The battery was originally developed for electric vehicle applications, but fell behind in the mid-1990s with the emergence of competing technologies such as the nickel–metal hydride. However, mega-watt installations still operate for power grid applications, the largest being a 34-MW/238-MWh (7 h) unit for the Rokkasho wind farm in Japan.

Replacement of the sulfur electrode in sodium–sulfur batteries with a cathode made of porous metal/metal halide impregnated with molten  $\text{NaAlCl}_4$  results in ZEBRA (Zeolite Battery Research Africa) batteries. The replacement renders it safer than the sodium–sulfur battery. The usual metal halides are  $\text{NiCl}_2$  and  $\text{FeCl}_2$ , yielding voltages of 2.58 and 2.35 V, respectively. The higher voltages translate to higher energy densities than that for the sodium-sulfur system. They also tolerate overcharge and over-discharge. ZEBRA batteries have been demonstrated for transportation and stationary applications. The present cost of these batteries is around \$500-600/kWh.

## 5. Electrochemical capacitors

### 5.1. Electrical double layer and pseudo-capacitors

The electrical double-layer at the electrode/electrolyte interface stores electrostatic energy like a capacitor. The energy stored per unit area in the interface became technologically attractive with the introduction of materials with high active-surface-areas, such as activated carbons. The two parallel regions of charge in the interface are in molecular dimensions of less than  $10^{-9}$  m. With carbons of surface areas of about  $1,000 \text{ m}^2/\text{g}$ , this creates a capacitor with specific capacitance of about  $10^5 \text{ F/kg}$  and possibly leading to devices rated at thousands of farads. Owing to their appreciably high capacitance, these capacitors are also referred to as supercapacitors or ultracapacitors. It is noteworthy that although supercapacitors are at least 10-fold lower in mass and volume, they have much slower response times, typically 0.3–3 s. This precludes their use in alternating current filtering applications, making them, unlike conventional capacitors, effectively direct current devices. Whilst the operation of EDLCs is based on non-faradaic accumulation of electrostatic charge at the electrolyte/carbon surface, fast faradaic charge-transfer brought about by the charging of the electrical double-layer at the electrode/electrolyte interface determines the working of pseudocapacitors. A combination of faradaic and non-faradaic components would generate electrochemical capacitors that exhibit high capacitance for pulse power as well as sustained energy; these electrochemical capacitors are referred to as hybrid supercapacitors.

Although power density values for a supercapacitor happen to be much higher than those for batteries, the latter have energy densities much higher than the electrochemical capacitors. Accordingly, electrochemical capacitors are categorized as power devices whilst batteries are energy devices. Typically, energy density values for an electrochemical capacitor are  $<10 \text{ Wh/kg}$  whilst energy densities for batteries could range between 30 and 200 Wh/kg. The absence of phase transformations and kinetic polarization limitations helps electrochemical capacitors to have much longer cycle life, typically about  $10^5$ , than batteries, typically 500–1,000. But response times for electrochemical capacitors are extremely fast in relation to batteries (about 30 s and more) where a 1s discharge time is equal to a 3,600 C-rate for a 1 Ah battery in battery terms. Supercapacitors also have lower operating voltages, limited by the breakdown potential of the electrolyte, than other type of capacitors, typically between 1–3.5 V per cell. In recent years, combinations of electrochemical capacitors and

batteries have been used in electric vehicles, where the former provides peak power for acceleration during hill climbing while the latter operates in a continuous low power-regime. The combined action improves reliability, longevity and performance of the power system.

Carbon-based electrochemical double layer capacitors exhibit high power densities (100–2,000 W/kg) but low energy densities (1–5 Wh/kg). Their typical discharge periods are between 1 s to 1 min. Since the charge and discharge processes are purely physical phenomena and involve no chemical changes, wear is low; they sustain hundreds of thousands of cycles and last for more than 15 years. They are especially suitable for instantaneous voltage compensation. Thus, batteries and electrochemical capacitors are complementary power sources. For example, in electric vehicle batteries can provide power for continuous drive while electrochemical capacitors can provide sudden bursts of power for acceleration and hill-climbing. The latter are also amenable to energy storage by regenerative braking.

Noble-metal oxides exhibit capacitances of about 700 F/g, but they are prohibitively costly and are sought to be replaced with transition metal oxides and non-oxides such as Ni(OH)<sub>2</sub>, MnO<sub>2</sub> and PbO<sub>2</sub>. Targeted research goals include increased lifetime, higher rated voltage, wider range of operating temperatures, higher combined power/energy density, and capacitance of the order of 1,000 F/g. Polymer-based supercapacitors, such as those based on bithiophene–triarylamine, are attractive as they give a peak specific capacitance of more than 990 F/g, but problems of swelling and contraction, leading to mechanical degradation and failure, as well as chemical degradation over repeated cycling must be addressed. Incorporation of CNTs in these electrodes can mitigate degradation caused by volume changes by reducing diffusion lengths. For example, a PANI/CNT composite electrode with a hierarchical porous nanostructure gave a specific capacitance of 1,030 F/g.

## 5.2. The lead–carbon battery-supercapacitor hybrid

The recognition that carbon added in small amounts (0.15–0.25 wt.%) into the negative paste of lead-acid batteries has been known to resist accumulation of lead sulfate led to a new class of energy storage devices: the lead–carbon asymmetric supercapacitors. The new configuration not only ensures higher cycle life, but also reduced sulfation of the positive electrode because of diminished swings in acid concentration during charging and

discharging. This system is also sealable like a VRLAB. Moreover, it can be operated over a wider depth-of-discharge window than conventional lead-acid batteries and can be charged and discharged at higher rates. The new technology can replace the conventional lead-acid system in applications such as in power grids. Its penetration is expected to be facilitated by the fact that essentially the same manufacturing infrastructure required for lead-acid batteries could be used for the new hybrid system.

## **6. Indian strength in battery R&D**

Given the versatility and varied chemistries that form the basis of practical battery systems, the available expertise can shape up into ideal technology platforms for forays into specific applications. India has a rich blend of expertise in the science and technology of electrochemical storage systems. The contributions from the Indian Institute of Science need special mention for realization of space-quality nickel–cadmium batteries at the Indian Space Research Organization and, in recent years, for up-gradation of lead-acid battery technology at NED Energy.

India boasts of world-class expertise in materials science and electrochemistry, vital for battery technology. However, efforts and funding for battery research have largely been piecemeal, which explains why no tangible products result from such programs. Today, a bulk of battery researchers has joined the bandwagon of lithium-ion batteries. Pockets specializing in lithium-ion batteries are the Central Electrochemical Research Institute, Karaikudi, Indian Institute of Science, Bangalore, Indian Institutes of Technology in Mumbai, Hyderabad and Kharagpur, Central Glass and Ceramics Research Institute, Kolkata, Pondicherry University, Puducherry, PSG College of Technology, Coimbatore and the Indian Institute of Science Education and Research, Thiruvananthapuram. Under the National Solar Mission project, CECRI is poised for a leap in its infrastructure for battery assembly and testing. The Indian Institute of Science is actively engaged in building a technology platform for storage batteries with its Energy Storage Systems Initiative. The International Advanced Research Centre for Powder Metallurgy and New Materials, Hyderabad and Naval Science & Technological Laboratory, Vishakhapatnam have also invested huge sums for lithium-ion battery research and development. Bharat Electronics Limited, Pune has also initiated some work in this area and Vikram Sarabhai Space Centre, Thiruvananthapuram is gathering

expertise to assemble space-grade lithium-ion cells up to 100 Ah. For research in lead-acid and nickel-iron batteries, only IISc can be counted upon. IISc has also successfully developed and demonstrated the first substrate-integrated lead-carbon hybrid ultracapacitor that has shown potential for commercialization. CECRI has acquired workable knowledge on nickel-metal hydride batteries. It should, however, be borne in mind that nickel-metal hydride batteries will become cost competitive to lithium-ion batteries only if India exploits its rich resources of rare-earth metals.

### **7. Multi-functionality in energy storage landscape**

Technological advances in areas as disparate as portable electronic gadgetry, electric vehicles and the electrical grid are often hamstrung by limitations of the power pack. Moreover, modern devices come with increasing multi-functionality. For example, today's mobile phones are transceivers of textual, voice and visual content with added capabilities for voice recording, photography, data storage and transmission, and multi-media entertainment. So much so, the power-on-demand profiles of applications become unpredictable, stretching over a large time scale as well as a large swathe of the energy/power spectrum. This requires power packs to be algorithm-controlled, multi-capable units with a balanced mix of batteries and electrochemical capacitors. Such battery-electrochemical capacitor combinations should effectively wrap up the entire energy-power-time range, helping to blur the restrictions imposed by Ragone plots. Such a judicious technology mix will also guarantee supply security and cost efficiency for a range of applications. Naturally, an area of research that is gaining momentum is asymmetric supercapacitor configurations that address the energy-power gulf between batteries and conventional capacitors. Specifically, these devices are based on large-area transition metal oxide electrodes that support rapid and reversible faradaic reactions in non-aqueous media that can operate at voltages much above 1.2 V.

### **8. New materials, new tools**

Approaches to battery systems with higher performance should focus on: (i) new materials and new chemistries, and (ii) improving the performance of existing systems. It is noteworthy that the push for batteries with higher energy and power densities would mean pushing the active materials and electrolytes to their stability limits. This also would mean a

penalty in terms of safety, reliability and charge-discharge cyclability, three crucial factors that determine the acceptability of the device. While higher energy densities would require any new battery-active material to possess higher specific capacities and/or to form galvanic couples with higher cell voltages, cell safety and durability would require more stable electrode-electrolyte interphases. Batteries exhibit high energy densities, but their power densities are low. By contrast, electrochemical capacitors have low energy densities, but high power densities. Thus, batteries and electrochemical capacitors complement each other in the energy-power equation. In addition, the latter deliver high pulse currents and sustain extended cycling. One way to enhance the energy densities of electrochemical capacitors is to resort to new materials with enhanced capacitive properties. However, a key priority in both the cases is the identification of highly conducting electrolyte solutions with wide electrochemical stability windows and capable of forming stable interphases with the active materials.

#### 8.1. Nano-architectures, an answer?

There is increasing evidence that electrochemical energy storage devices stand to gain from the rapidly strengthening nexus between electrochemistry and nanoscale science. A notable feature of this nexus is that a number of materials that have hitherto been dismissed as electrochemically inactive are now emerging as hot favourites to replace existing active materials in batteries. Particular mention must be made of the demonstration of nano-SiO<sub>2</sub> and nano-SiC as potential low-cost and high-capacity anode materials in lithium-ion batteries. Conversion electrodes are another class of such materials that hold promise as anodes that can deliver multiple electrons per molecular unit of the active material. Such discoveries have opened the floodgates for systems that are projected as 'beyond lithium' and 'beyond intercalation chemistry.' The combination of electrochemistry and nanoscale materials chemistry has also triggered research into pseudo-capacitance charge storage materials. In fact, studies with nanostructured materials have led to the possibility of moving towards the upper right quadrant of the Ragone plot, which erases the demarcation of 'batteries for energy' and 'capacitors for power' model.

Tailored, multi-functional nano-architectures can enhance performance by way of improved electronic and ionic conductivities, diffusion and mass transport, and electron

transfer and electrocatalysis. Due to their high surface areas, nanostructured materials can support high electrode reaction rates, which should translate to high power capabilities. Moreover, because such structures present reduced diffusion lengths, the time constant for diffusion of active species can be brought down considerably. Although the high porosity of such materials should facilitate ingress of electrolyte into the interior of the electrode structure, it can reduce volumetric energy densities. Another disadvantage of nanostructured electrode materials is that due to enhanced surface energies, they facilitate undesirable reactions with the electrolyte, leading to extensive passivation, self-discharge, and truncated cycling/calendar life. While nanoscopic materials do promise high-performing devices, their suitability for energy storage hangs on our understanding of phenomena that occur at the nanoscale.

It is clear that the ability to control matter at the nanoscale is becoming an additional functional variable in our search for high-performance materials for electrochemical devices. But that introduces more questions particularly relating to co-existence of nanoscale phases, role of surface energy on electrochemical properties, electrolyte structure in confined spaces, structure of surfaces at the nanoscale, effect of nano-dimensions on electronic properties, delineation of pseudocapacitive behaviour from faradaic reactions at the nanoscale, and inter-relationships between electron and ion transport in nanostructures.

## 8.2. Theory and modeling

In contrast to their simplicity in appearance, batteries and electrochemical capacitors are complex systems with a multiplicity of reactive and passive components and interfaces. The performance of the device is thus limited by their properties. A theoretical understanding of the charge transfer phenomena in correlation with experimental results remains a large gulf that must be bridged. There are also limitations brought about by mass and charge transport, and their dependence on design and structural parameters. For example, the interplay of pore size, pore morphology and pore distribution on mass/charge transport, and electrolyte behavior in confined spaces are poorly understood. Modern analytical and characterization tools, including *in situ* microscopic and spectroscopic tools, can help unravel the complex molecular-level phenomena that underlie individual charge-transfer processes and the nature and properties of dynamically changing solid electrolyte interphases. Any insight thus gained

on the working and failure mechanisms, backed by sound computational modeling and simulation can lead to electrode materials, electrode architectures and system designs for next-generation storage devices.

## 9. Technology readiness level

The technology readiness levels (TRL) of the different electrochemical storage systems can be evaluated based on a metric as under.

- (i) innovation (TRL 1–3) [TRL 1: basic research; TRL 2: applied research; TRL 3: critical function or proof-of-concept established].
- (ii) emerging technologies (TRL 4–6) [TRL 4: laboratory testing/validation of component(s)/process(es); TRL 5: laboratory testing of integrated/semi-integrated system; TRL 6: prototype system verified].
- (iii) system integration (TRL 7 and 8) [TRL 7: integrated pilot system

Table 2. Technology readiness levels for different electrochemical energy storage systems.

System	Projected energy/power density at system level	TRL	Major issues/limitations
Advanced lead-acid	25–40 Wh/kg 75–300 W/kg	>9	Low energy density.
Nickel–iron	30 Wh/kg 55 Wh/l	7	Gassing; low charging efficiency.
Iron–air	500 Wh/kg 700 W/l	1–3	
Nickel–metal hydride	70 Wh/kg 120 Wh/l	7–9	
Lithium-ion	150–200 Wh/kg 250–300 Wh/l	7–9	Safety.
Lithium–sulfur	400 Wh/kg 600 Wh/l	4–6	Cycle life; polysulfide formation.
Sodium–sulfur	150–240 Wh/kg 150–130 Wh/l	7–9	
ZEBRA	100–120 Wh/kg 150–200 Wh/l	7–9	
Vanadium flow cell	10–25 Wh/l	7–8	Low volumetric energy density.
Soluble lead flow cell	5 Wh/l	4	Low energy efficiency.
Electrochemical double layer capacitors	1–5 Wh/kg 100–2,000 W/kg	4–6	
Supercapacitors	1–10 Wh/kg 1–2,000 W/kg	4–6	
Lead–carbon hybrid	1–2 Wh/kg 1,000 W/kg	4–6	

demonstrated; TRL 8: system incorporated in commercial design].

- (iv) market penetration (TRL 9) [TRL 9: system proven and ready for full commercial deployment].

Under the aforesaid metric, the TRLs of the systems discussed above are indicated in Table 2, which factors in the current status of each technology and what can be achieved.

## 10. Recommendations

The committee after careful deliberations has made the following recommendations:

1. Establish an R&D programme, initially with an annual fund of Rs. 100 crore, to support research projects in energy storage devices. The programme should fund basic, directed basic and applied research projects at academic institutes, universities and research institutes, both in public and private domains, as well as public and private sector industries. In the academic institutes, the research projects should specifically focus on high-risk basic and platform technologies, whereas the industry should focus on technologies for commercialization, ploughing in a part of its funds into research. As a general enabler, the government should provide directions and funds for basic research, platform technologies, infra-structure building, and even disruptive and tangential research. Multiple funding with multiple approaches should be encouraged to provide a smorgasbord of options to choose from. Efforts should be made to encourage an integrated consortium approach with expertise drawn from seemingly disparate disciplines.
2. Establish centrally funded centers for research into select electrochemical energy storage systems on a cooperative model of partnership with the industry, each specializing on one system (iron-based accumulators, lead-carbon hybrid battery, futuristic systems, supercapacitors). Besides developing specific technologies, each centre shall act as a knowledge repository of developments in the specific area. These centers shall work on a hub-and-spoke model, tapping on and benefiting from discrete knowledge from across the country. Any generic knowledge generated at the centers of battery research should be available to all. Intellectual property rights should, however, be owned by the center, with the rights transferred to the industry either on an exclusive or non-exclusive manner. A

suitable model may be established for sharing the funding requirement of the centers between industry and government. The Committee recommends establishment of such centers at CECRI, Karaikudi (for iron-based accumulators), IISc, Bangalore (for lead-carbon hybrid battery) and ARCI, Chennai (for lithium-based batteries), with each center also pursuing activities on related supercapacitor systems.

3. In view of the increasing growth and demand of lithium-ion batteries and the absence of manufacturing facilities in the country, industries may be encouraged to initially import the subcomponents, and to assemble and market. The import of subcomponents may be exempted from duties to encourage Indian industry to enter into manufacturing and progressively initiate backward and forward integration. Such duty-free imports may be limited to a specified period so that there will be pressure on the industry to quickly implement the entire manufacturing process. This measure will significantly reduce the imports and create manufacturing capabilities in the country.
4. Develop human resources in energy storage devices. India will need qualified human resource to establish the necessary expertise in carrying out translational research and for absorbing imported technologies. Therefore, the chosen CoEs should endeavour to develop human resource required in energy storage devices, offer academic programs in association with a local university and conduct refresher courses for the industry. Furthermore, the center should facilitate exchange of experts with other institutions/industry to encourage cross-fertilization of ideas as well as pursue international collaborations. Besides, the center should organize periodic conferences for dissemination of related knowledge, serve as a springboard for new technologies and as a cradle of personnel skilled in energy devices and management.
5. Although the present initiative by the Office of the Principal Scientific Advisor is system-oriented and not application-oriented, NMEM 2020 merits special focus. By 2020, India will have 5–6 million vehicles on the road, most of which would be two-wheelers. Therefore, R&D activities in the country should largely focus on

grand challenges in electric mobility with special reference to batteries. Therefore, research in EV batteries should target fast charging, range anxiety, cost-effective battery management systems, safety concerns including internal shorts, battery combinations (combo power scheme), etc. NMEM 2020 should be juxtaposed with India's Solar Mission program so that a large swathe of the country's vast solar potential is tapped for transportation (through battery charging stations). Both AC charging (from the convenience of the mains supplies at home, with a built-in rectifier in every car) and DC charging (at public charging stations, with large battery banks) must be encouraged. Until full reliance on indigenous resources is realized, the government should give tax benefits to the industry for import of subcomponents.

6. The role of active materials and interfaces in the working and failure of batteries is becoming clearer. Passive components such as battery casing, separators, tabs, current collectors, etc. require personnel with different academic backgrounds. The not-so-straightforward design aspects required to ensure safety of devices packed with highly energetic materials, often in contact with flammable electrolyte solutions, must also be addressed. Much needs to be done to ensure good heat dissipation and to manage inadvertent electrical/mechanical abuse conditions, which call for expertise in thermal management and power control systems. Since applications go far beyond the simple cell/battery pack, a variety of skills need to be yoked in to realize a battery module that fits the application. For example, the requirements for photovoltaic applications are different from those for electric traction; so are those for load-leveling and micro-grid stations. The program should, therefore, be multi-pronged and integrative, drawing on expertise from disparate groups, but working under a nodal center that directs the national activity.

## **11. Looking ahead**

Given their critical role in energy security and in reducing greenhouse gas emissions, electrochemical energy storage should be a prime objective for policy makers. Large-scale economical storage of electrical energy for applications ranging from portable gadgets to

transportation, power grid and beyond remains a great challenge and our weakest link to the future. Electrochemical storage technologies provide solutions for decentralized units as well as for stationary use. While their portability guarantees a niche market for them, competition can arise from other energy storage technologies for large-scale, stationary applications. It is thus necessary to reduce capital cost and to enhance the service life and reliability of electrochemical energy storage systems. Mature technologies such as those of lead-acid and nickel-metal hydride batteries may soon be replaced by those of advanced lead-acid and lithium-ion batteries in the near term. Second-generation nickel-iron, lead-carbon hybrid and flow batteries should be able to meet the storage requirements in the mid-term. Emerging technologies such as lithium metal polymer batteries, lithium-sulfur and lithium-air systems are expected to blossom only in the long term. In order to ensure that such technologies measure up to the demands of a developing nation like India, cross-cutting research must be undertaken with special emphasis on the synthesis and characterization of multi-functional and nanostructured materials, and high-performance electrolytes, backed by sound theory of the physico-chemical phenomena and processes that occur at the molecular scale in these systems. Experience tells that uninterrupted power supply systems and power trains supported solely by batteries have not proven to be complete solutions due to shortcomings such as relatively low power density and cycle life of batteries. Coupling supercapacitors with batteries could address this long-standing issue.

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