Review Article

Electrochemical Energy Storage Devices

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Increasing reliance on renewable energy sources, and technological advances in areas such as electric traction, smart grids and portable electronic gadgets have catalysed renewed interest in electrochemical energy storage options, of both miniature and large scale. The electrochemical mode of energy storage offers flexibility and scalability as well as candidate systems with a range of energy 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. In this study, we assess the suitability of both mature and emerging electrochemical storage technologies that can meet the energy requirements of India.

Keywords: Energy Storage; Batteries; Electrochemical Capacitors; Energy Sustainability; Renewable Energy

Introduction

With the world electricity consumption expected to grow at 3.6% annually (engineeringnews.co.za, 2009), increasing emphasis is placed on more efficient technologies with low or zero-carbon footprints for both generation and use of energy. Since a key requirement of the grid distribution system is a balance of the amount of electricity fed into it and the demand, electrical storage technologies are called upon for both storing excess power and for meeting peak demands. The balancing act between supply and demand needs a re-look as we prepare to move from conventional power plants that depend, for example, on the fast-depleting oil to renewable energy sources such as those based on the wind and the sun. However, energy production by renewable technologies is weather-dependent and, therefore, unpredictable. Storage and release of electrical energy is critical for uninterrupted and non-fluctuating supply with increasing penetration of intermittent renewable power sources. However, there is only a handful of back-up storage technologies

that 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 hydro storage (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. Most importantly, they must also have low rates of self-discharge. Flywheel and superconducting magnetic energy storage

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technologies suffer from self-discharge rates of 3-20% per hour and about 12% per day, respectively. In 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 allows for flexibility in deployment, which can in turn facilitate widespread use and networking of intermittent renewable energy technologies. Electrochemical storage technologies are ideal for transportation where instant power should be available to the vehicle for reasonable lengths of time. They are mature, inexpensive and ensure high levels of safety, reliability and durability. They are also ubiquitous, available in various sizes and capacities, suitable for stationary and portable applications in a broad spectrum of human activity.

Electrochemical Energy Storage Systems

Two types of electrochemical energy storage systems can be recognized: (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 everyday requirements, for example, 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

processes that govern their operation, performance, safety limits and failure is 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. Here, 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 both mature and emerging (European Parliament's Committee on Industry, Research and Energy, 2008; Soloveichik, 2011; Pollet *et al.*, 2012), suitable for a sustainable future, and adequate enough to meet the needs of the Indian populace. Table 1 compares the features of select battery systems.

Battery Systems

Lead-acid Batteries

Lead-acid batteries are unrivalled in terms of cost-effectiveness with less than $150/kWh. It commands more than half of a whopping $60 billion world battery market, with India's share of the market being $4 billion. The most common use of these batteries is for starting-lighting-ignition (SLI) in automobiles. The

Table 1: Features of select battery systems

System		Cell voltage (V)	Energy density (Wh/kg)	Cycle life	Self-discharge/ month (%)	Major issues/limitations
Lead-acid		2.04	25-40	200-300	5	Low energy density
Nickel-cadmium		1.2	45-80	1000	15-20	Cadmium toxicity
Nickel-metal hydride		1.2	70	300-500	20-30	Cost of rare earth metals
Nickel-iron		1.37	30	3000	30-50	Gassing; low charging efficiency
Lithium-ion	cobalt	3.6	150-190	500-1000	5-10	Safety
	manganese	3.8	100-135	500-1000	5-10	Poor performance above 55C
	phosphate	3.3	90-120	1000-2000	5-10	
Sodium-sulphur		1.78-2.08	140-170			

Note: Cycle life is defined here as the number of complete charge-discharge cycles that a battery can sustain before its capacity drops below 80% of its original capacity

battery operates on the double sulphate 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 sulphate. Their cycle life and deep discharge capability depend on the type of construction.

A mature technology, the lead-acid battery is backed by 150 years of development. Contrary to what some believe, 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 can also lead to corrosion of the positive plate. High-rate recharge and failure to routinely return to full state-of-charge can lead to sulphation of the negative plate. In stationary applications such as power grids and roof-top photovoltaic installations, less taxing regimes may be expected.

Commercially available lead-acid batteries have energy densities of 25-45 Wh/kg. Their discharge-charge efficiencies lie between 60% and 95%. Although their current energy densities are rather low and their cyclability only of the order of a few hundreds of cycles, they are the choice workhorse for a variety of applications where weight and bulkiness are secondary. The flooded-electrolyte lead-acid batteries are the traditional types used in stationary applications although the valve-regulated lead-acid batteries (VRLABs) are now increasingly being used. The VRLABs use a recombination mechanism by which the oxygen evolved at the positive plates combine with the hydrogen evolved on the negative plates to form water; this provision eliminates the need for periodical 'topping' and allows a sealed construction. These batteries use an absorbent-glass-mat or a gelled mass as the electrolyte and have a compacted stack construction. VRLABs exhibit specific energies of 35-40 Wh/kg and 70-80 Wh/l, and energy and power efficiencies of 95% and 75%, respectively. Their self-discharge rates are only 2-5% per month. Improvements in design and use of alloying additives have resulted in VRLABs with a shelf-life of 8 years and a cycle-life of over 1,000 cycles.

As noted earlier, the science and technology of lead-acid batteries is undergoing a tremendous 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 sulphation, which is now sought to be mitigated by use of a thin layer of carbon in the negative plate (Kelley and Taylor, 2006). 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. Lead-acid batteries continue to cater to emerging demands for portable or reserve energy sources by novel technological innovations and/or design solutions for their production. Other advantages include an operation temperature of –20ºC to +50ºC, and availability of technologies to recover 99% of lead from spent batteries. Key disadvantages such as relatively poor cycle-life and limited specific energy have, however, restricted their wider commercial adaptability.

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, invented by Thomas Alva Edison in the USA as early as 1901, was extensively deployed in the railway carriages of the erstwhile Soviet Union. The instability of the iron electrode in alkaline medium and the lead-acid battery lobby put the lid on the nickel-iron battery technology.

However, in recent years, interest in nickel–iron batteries is being revived since these batteries are reliable and inexpensive. They can be subjected to high discharge rates, exhibit good low- and high-temperature behaviour with long cycle life, undergo two-step charge-discharge and provide reserve charge during the second step of discharge. These batteries are electrically and mechanically rugged, and, above all, environment-friendly. The nickel-cadmium system, developed by Waldemar Jüngner, and made maintenance-free and sealable by Neumann *et al.* (Varta Batterie, 1982), 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 the memory effect. (Memory effect is a self-conditioning, reversible phenomenon by which nickel-cadmium cells appear to adjust their electrical properties to a certain duty cycle to which they have been subjected to for extended periods of time. It leads to a temporary and partial loss in capacity. In other words, the cells deliver less capacity than they are designed for. Memory effect is observed in cells with sintered-type cadmium negative electrodes.) 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 of the production of nickel-cadmium batteries worldwide. Advances in the technology of the nickel-zinc system are hampered by the poor cyclability of the zinc anode, primarily due to non-uniform zinc deposition upon recharge. In contrast, nickel-metal hydride batteries have shown promise in hybrid electric vehicles albeit being expensive and prone to heavy self-discharge.

Nickel-iron Batteries

In hibernation for decades, due to euphoria generated by rapid strides in competing battery systems, 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 have now been successfully 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. 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 a given considering its longevity (typically 3000 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.

Nickel-metal Hydride System

Cadmium being toxic, alternatives to the nickel-cadmium system began to be explored, which resulted in the nickel-metal hydride system (Willems, 1984; Ogawa *et al.*, 1988). The nickel-metal hydride battery uses alloys of AB_2 composition (A: drawn from Ti, V, Zr, etc.; B: Ni, Co, Cr, Mn, Al, Sn, etc.) and AB_5 compositions (A: La, Ce, Pr, Nd, or misch metal; B: Ni, Co, Mn, Al, etc.) as the anode. Improvements in the technology include use of a new A_2B_7 composition and PEO-KOH-gelled electrolyte that ensure 80% coulombic efficiency (Vassal *et al.*, 1999). Although nickel–metal hydride batteries have been popular power sources for consumer electronics, particularly in portable gadgets such as cameras, cell phones and laptops, and for electric traction, it is only recently that they began to be considered for uninterrupted power systems and telecommunication (Zelinsky *et al.*, 2010). However, the discharge-charge efficiency is only about 70%. Perhaps the one factor that stands against this system is its cost, which is about twice that of lithium-ion batteries. However, if the metals, especially the rare earths can be sourced locally, defunct nickel-cadmium manufacturing plants can be re-activated to suit this system. The metal components in these batteries must be recycled for sustaining this metal-rich technology as recovery procedures for nickel from spent batteries are already established.

A major disadvantage of nickel-metal hydride batteries is their high rate of self-discharge (typically 30% per month). Both nickel-metal hydride and nickel-cadmium systems have similar cell voltages, although the former does not exhibit memory effect. They have moderately high specific energies and tolerate temperatures up to 70ºC, 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. 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 prevented its widespread use 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.

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 ten year service in automobiles and more than 200,000 running kilometres. Developments in this direction include replacement of the sintered nickel electrode with a foam electrode, bringing about ~50% improvement in volumetric capacity. Recent adoption of 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.

Metal-air Batteries

A clear advantage of rechargeable metal-air batteries over conventional systems is that only one reactant, namely, the anode material, needs to be contained within the battery, while oxygen, the active material for the cathode, is sourced from the atmosphere. Thus, the energy densities of metal-air batteries can be high, between 110 and 420 Wh/kg (itpower.co.uk). A notable disadvantage of metal-air batteries, however, is their poor energy efficiency (around 50%). Research emphasis today is to move from the mechanically rechargeable version to the electrically rechargeable version. The latter version may have a lower specific energy, but has the advantage of lower life-cycle costs. The electrically rechargeable version may have a bi-functional cathode or an auxiliary (third) electrode, which is used only for recharging the battery. Metal-air batteries based on aluminium are purely mechanically rechargeable, while those based on zinc and iron are potentially electrically rechargeable. Considerable efforts are in progress to develop lithium-air rechargeable batteries with an open-circuit voltage of 3.86 V.

Recharging of the zinc electrode is fraught with problems of non-uniform deposition and shape change associated with precipitation, crystallization and grain growth. Two companies have in the recent past claimed to have developed a technology for long-cycling zinc-air cells and are planning large-scale production (phys.org, 2012; treehugger.com). While they are in common use in a variety of portable applications (e.g., earphones, wrist watches), zinc-air batteries are projected as ideal low-cost options for grid storage and for vehicular traction. They are safe to use and their constituents recyclable.

Unlike the zinc electrode, the iron electrode does not suffer problems of redistribution of active materials or gross shape change upon prolonged electrical cycling. The theoretical specific energy density of the iron-air system is 955 Wh/kg, which is about thrice that of nickel-iron batteries. 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.

Lithium-ion 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 carbon. The working principle of the lithium-ion battery is unlike that of conventional batteries, and is schematically described in Fig. 1. These batteries represent the cutting edge of electrochemical science and technology today. Bestowed with the highest energy densities (150 Wh/kg and projected to reach 200 Wh/kg with the introduction of nanocomposite electrodes (ntrc.itrc.org, 2004)), 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 reduced 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 salts can also be recycled although their content in lithium-ion batteries is below 1% by weight (Shukla and Kumar, 2013a).

Current technologies aim at replacing the toxic and expensive cobalt in the electrodes with low-cost and environment-friendly metals such as iron, manganese, titanium, etc. Low-cobalt alternatives include $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, spinel electrode materials such as the high-

voltage $LiNi_{0.5}Mn_{1.5}O_4$ and olivines such as $LiFePO_4$ and $LiFe_{0.8}Mn_{0.2}PO_4$. A major breakthrough was made by the introduction of $LiFePO_4$ as the cathode and $Li_4Ti_5O_{12}$ as the 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. Lithium-ion batteries have now become commonplace and are the choice systems for grid storage, telecommunication and photovoltaic applications.

New chemistries based on lithium are emerging, which include the lithium-sulphur and lithium-air systems. A practical energy density of 350 Wh/kg has already been demonstrated for the lithium-sulphur system (Mikhaylik *et al.*, 2008). The lithium-sulphur 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 an energy density of 1,000 Wh/kg (Kumar *et al.*, 2010). 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
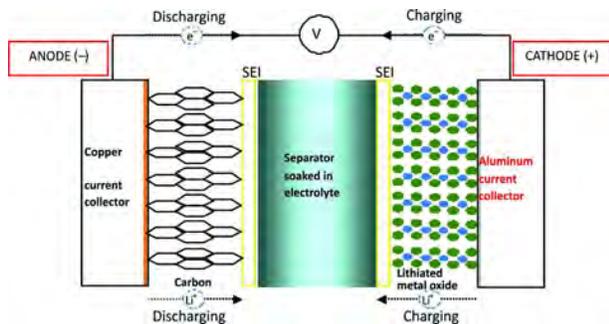

Fig. 1: Working principle of a lithium-ion battery

methodologies based on shutdown separators and electrical/pressure interrupts, manufacturers depend 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.

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. As 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–acid flow battery are among candidate systems that must be pursued. The electrode reactions in the soluble lead-acid flow battery are the same as in the lead-acid battery. However, unlike in the other redox flow systems, one needs to employ only an undivided cell here. This is because both charged products (Pb and PbO_2) are insoluble while soluble discharge product (lead methanesulphonate) is common for both the electrodes.

Sodium-sulphur and ZEBRA Batteries

The key to success of the molten sodium-based batteries is a solid membrane of β-Al_2O_3 (often doped with Li^+ or Mg^{2+}) with excellent sodium ion conductivity at elevated temperatures. Operating at 300-350ºC, the sodium-sulphur battery gives an energy density of 140-170 Wh/kg at an average voltage of 1.78-2.208 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 sulphur electrode in sodium-sulphur batteries with a cathode made of porous metal/metal halide impregnated with molten $NaAlCl_4$ results in ZEBRA (Zeolite Battery Research Africa) batteries. The replacement renders it safer than the sodium-sulphur battery. The usual metal halides are $NiCl_2$ and $FeCl_2$, yielding voltages of 2.58 and 2.35 V, respectively. The higher voltages translate to higher energy densities than that for the sodium-sulphur system. They also tolerate overcharge and over-discharge. ZEBRA batteries have been demonstrated for transportation and stationary applications. The capital cost of these batteries is around $500-600/kWh.

Electrochemical Capacitors

Electrical Double Layer and Pseudo-Capacitors

Energy and power play against each other. Therefore, increasing one will lead to a loss in the other. This means that if we require high power from the battery, we will extract less total energy than when we require low power. Capacitors complement battery power by allowing very rapid charge and discharge cycles. Accordingly, capacitors will gel well with batteries into the emerging energy-storage landscape. As the capacitance mode allows storage of electricity directly as electrical charges, electrical double layer capacitors can have efficiencies close to 100%. 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 and 1 min. Because 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 vehicles, 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. (In regenerative braking, the kinetic energy of a slowing vehicle is converted into electricity by recharging the car's battery. In conventional cars, the brake pads clamp down on the wheels and let the kinetic energy dissipate as heat. In regenerative braking, an electric motor is used to slow the car slow down. In other words, the flow of power through the electric motor is reversed to slow the car down, effectively converting the motor into an electric generator to charge the battery).

Charge storage by the pseudo-capacitance mode is another method of capacitive storage. A combination of faradaic and non-faradaic storage, as in supercapacitors, should, therefore, result in high pulse power with continuous energy (Ravikumar *et al.*, 2009). Noble-metal oxides with capacitance of about 700 F/g are now employed in supercapacitors. Owing to their prohibitive cost, they are sought to be replaced with transition metal oxides and non-oxides. Nano-structures of $Ni(OH)_2$, MnO_2, PbO_2, etc. are also being investigated (Choi *et al.*, 2006; Naoi and Simon, 2008; Banerjee *et al.*, 2012). 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 1000 F/g. Non-aqueous lithium-ion hybrid supercapacitors with operating voltages as high as 3.5 V are also on the horizon. Polymer-based supercapacitors such as those based on bithiophene-triarylamine, are attractive as they provide 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 provided a specific capacitance of 1030 F/g.

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 sulphate (Shiomi *et al.*, 1997), led to a new class of energy storage devices: the lead–carbon asymmetric supercapacitors (Lam and Louey, 2006; Lam *et al.*, 2007). The new configuration not only ensures higher cycle life, but also reduced corrosion of the positive electrode because of diminished swings in acid concentration during charging and discharging. This system is also sealable similar to a VRLAB, with oxygen recombination efficiently supported by the carbon negative electrode. 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 those of 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.

Multi-functionality

Technological advances in areas as disparate as portable electronic gadgetry, electric vehicles and the electrical grid are often hindered 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. Furthermore, 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 (Fig. 2). 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.
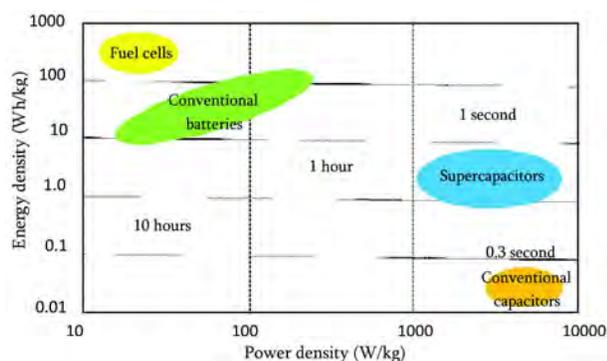

Fig. 2: Ragone plots for batteries, capacitors and fuel cells

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 (Shukla and Kumar, 2008). 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. In 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.

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 demonstration of nano-SiO_2 (Chang *et al.*, 2012) and nano-SiC (Kumari *et al.*, 2013) 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 (Poizot *et al.*, 2000; Tarascon *et al.*, 2005). 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. 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 through improved electronic and ionic conductivities, diffusion and mass transport, and electron transfer and electrocatalysis (Shukla and Kumar, 2013b). 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 higher 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. However, 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.

Theory and Modelling

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 behaviour 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 modelling simulation can lead to electrode materials, electrode architectures and system designs for next-generation storage devices.

The Road Ahead

It is necessary to introduce a policy on sustainable energy with stakeholders drawn from the academia, industry and government. The academia and R&D institutions should lay the seeds of technology independently or in partnership with industrial houses. Their research programs should specifically focus on high-risk basic technologies and platform technologies. The industry should focus on technologies for commercialization, allocating a part of its funds into research. In addition to devising business strategies for its growth, the industry should advise the government on emerging trends in the application sector. As a general enabler, the government should provide directions and funds for basic research, platform technologies, and infra-structure building, and even disruptive and tangential research.

India will need to establish the necessary expertise in carrying out transformational research and for absorbing imported technologies. A careful revamping of the syllabi at the university level is thus called for. Another strategy would be to establish centres of excellence in electrochemical power systems across the country, where services of people with proven/potential expertise can be tapped.

Conclusions

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 both 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 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-sulphur 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 such as 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.

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