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Electrochemical energy storage systems: India perspective

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Abstract. Design and fabrication of energy storage systems (ESS) is of great importance to the sustainable development of human society. Great efforts have been made by India to build better energy storage systems. ESS, such as supercapacitors and batteries are the key elements for energy structure evolution. These devices have attracted enormous attention due to their potential applications in future electric vehicles, smart electric grids, etc. This paper first addresses the fundamental principles, structure and classification of supercapacitors and batteries, and then focus on the recent advances on these devices made by India especially from Centre for Materials for Electronics Technology (C-MET), a scientific society under the ministry of electronics and information technology, government of India. Also the current global market scenario and market in India are also discussed in detail to recognize the most appropriate energy systems for the emerging economy like India.

Keywords. Energy storage; alternative energy; supercapacitor; battery .

1. Introduction

Globally, almost 1.2 billion people do not have access to electricity. The traditional centralized grid has failed to provide basic cost-effective electricity to underserved population. The remote and distributed power systems, though have various challenges, are considered to be a potential option for service. International Energy Agency (IEA) has estimated that the developing countries require doubling their energy requirement by 2020. The 80% of the total energy will be produced and consumed by these nations during 2035. The increasing pollution, global warming and geopolitical concerns as well as rising fuel cost are forcing the nations to find out alternative to fossil fuels. The renewable sources of energy are the only green alternative means to cater this need. The cost of renewable energy sources like wind or solar power is falling significantly over the decades. However, they are not available all the time and hence, the effective and efficient energy storage systems are highly desirable for providing sustainable service, especially in the zone of weaker grid infrastructure region.

Energy storage market globally is expected over 40% annual growth in the upcoming years. Consequently, storage systems with high energy density and high power are in demand. To address this issue, a more extensive use of renewable sources and efficient transportation systems are needed. Energy storage technologies play an important role in emerging economies by integrating renewable energy and improving the quality of the electricity supply [1]. This paper has attempted to study all the available storage systems, their specifications and merits to understand the most suited solution for the promising economy like India. This paper has also attempted the recent R&D initiatives to address the technical challenges faced by storage devices.

2. Energy storage systems

Currently four types of energy storage systems (ESS) are available, which are discussed here in detail.

2.1 *Mechanical energy storage*

In these systems, the energy is stored as potential or kinetic energy, such as (1) hydroelectric storage, (2) compressed air energy storage and (3) fly wheel energy storage. Hydroelectric storage system stores energy in the form of potential energy of water and have the capacity to store in the range of megawatts (MW). However, a major challenge is the availability of proper location. In case of compressed air energy storage, the kinetic energy of the compressed air is used to store energy. This technology is limited by infrastructure issues as the plant required to store compressed air underground. Flywheel energy storage system stores energy in the form of kinetic energy where the rotar/flywheel is accelerated at a very high speed. It can store energy in kilowatts, however, their designing and vacuum requirement increase the complexity and cost.

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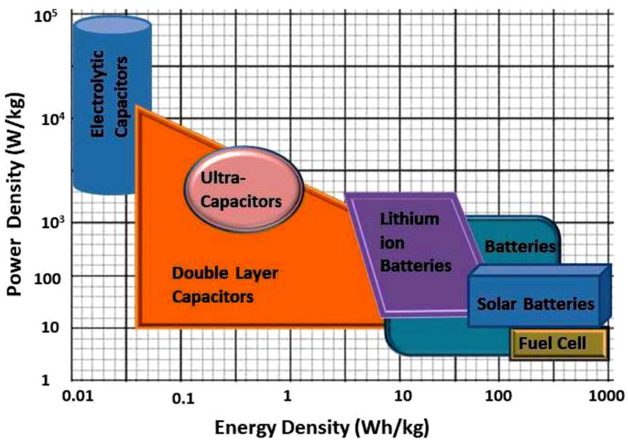

Figure 1. Ragone plot showing energy *vs.* power density for different power devices [1].

2.2 *Electrochemical energy storage*

In this system, energy is stored in the form of chemicals. They include both batteries and supercapacitors. Batteries can be primary or secondary based on the chemicals used, such as lead acid, nickel-electrode, lithium-ion, sodium–sulphur, sodium nickel chloride, zinc–bromine, polysulphide-bromide, and vanadium redox. Ragone plot (figure 1) shows comparison between batteries based on their energy density and power density [1].

Another type of electrochemical storage system is supercapacitor. Supercapacitors can provide high power compared to batteries, but unable to store charge like batteries. Hence, supercapacitors are used where high power is needed and not higher energy capacity [2]. Supercapacitors and batteries are combined together to provide hybrid energy storage systems. The power output of supercapacitors is lower than electrolytic capacitors, however, their specific energy is higher than the capacitors [3] (table 1). Supercapacitors fill the gap between aluminium electrolytic capacitors and batteries as shown in a Ragone plot (figure 1).

2.3 *Thermal energy storage*

A thermally insulating chamber is used where energy is stored as heat by heating up medium like water. As it requires storing chambers, infrastructural investment is the major disadvantage.

2.4 *Superconducting magnetic energy storage*

Superconducting magnetic energy storage system stores energy in the form of magnetic field. This magnetic field is generated when direct current flows through the coil. Its advantages include no losses due to no resistance. However, it suffers from the requirement of low temperature for operation and complex systems.

3. Supercapacitors

Supercapacitors store energy electrostatically or faradically. They have higher power densities, cyclic efficiency, cycle life and portability. They can be classified based on charge storage mechanisms (figure 2).

3.1 *Classification of supercapacitors*

3.1a *Electric double layer capacitors (EDLC)*: EDLC type supercapacitors store charge electrostatically i.e. through non-faradic process. The electrochemical double layer is formed when voltage is applied. Charges are accumulated on electrode surfaces. Hence, no charge transfer takes place between electrode and the electrolyte.

Due to potential difference, ions diffuse through electrolyte to the oppositely charged electrodes. Many different types of materials are used for EDLC type systems, such as carbon nanotubes, graphene and activated carbon.

3.1b *Pseudocapacitive type supercapacitors*: Pseudocapacitors also store charge through faradic process [5]. When potential is applied, the redox occurs on surface of electrodes. Transfer of charges across double layer results in faradic current passing through the cell. Compared to EDLCs, pseudocapacitors can provide higher specific capacitance and energy densities. Following types of materials are used in pseudocapacitive type storage:

Table 1. Comparison of electrochemical energy storage technologies [4].

Characteristics	Capacitors	Supercapacitors	Batteries
Specific energy (Wh kg^{-1})	<0.1	1–10	10–100
Specific power (W kg^{-1})	>10,000	500–10,000	<1000
Discharge time	$10^6 - 10^3$	S to min	0.3–3 h
Charge time	$10^6 - 10^3$	S to min	1–5 h
Coulombic efficiency (%)	About 100	85–98	70–85
Cycle life	Almost infinite	>500,000	About 1000

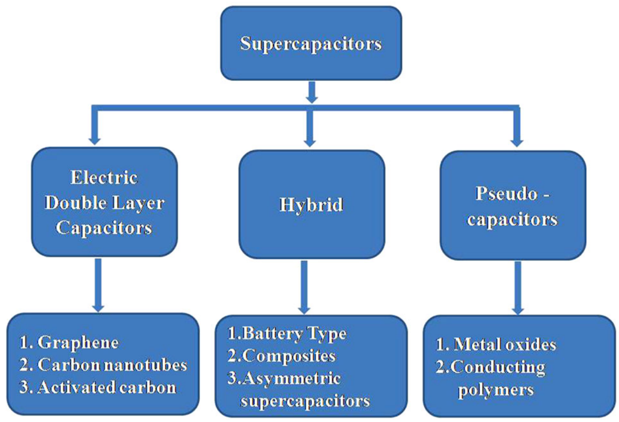

Figure 2. Classification of supercapacitors [5].

- Metal oxides: (SnO_2, RuO_2, NiO, MnO_2, $NiCo_2O_4$, $MnCo_2O_4$).
- Conducting polymers: PANI (polyanaline), polypyrole.

3.1c *Hybrid*: The hybrid system combines two different types of energy storage systems, such as battery-like and capacitor-like electrodes in the same cell. One of the electrodes shows EDLC type and another as pseudocapacitor type behaviour. Three different types of hybrid systems are present:

Composite: Composite electrodes have both carbon-based metal oxides or conducting polymers type materials in a single electrode. Hence, one single electrode can have both physical and chemical charge storage mechanisms. Nanocomposites like CNT/PANI are hybrid composites, where CNT with double-layer of charge and high-specific surface area improves the contact between pseudocapacitive materials and electrolyte.

Battery type: Battery-type hybrid combines both supercapacitor and battery-type electrodes. Hence, one cell can provide characteristic properties of both of them. Lithium ion capacitors use EDLC carbon and carbon doped with lithium ions electrodes to give high-specific power and energy density.

Asymmetric hybrid: Asymmetric hybrid involves both EDLC and pseudocapacitor-type electrodes. Recently, capacitor with activated carbon and an ACF–polyaniline composite with H_2SO_4 solution as an electrolyte has been developed. This capacitor shows voltage upto 1.6 V and high energy densities of 20 Wh kg^{-1}, power densities of 2.1 kW kg^{-1}, cycle lifetime of 90% during the first 1000 cycles and high coulombic efficiency [6]. Such type of supercapacitors exhibit higher voltage and higher specific energy.

3.2 *Current trends in supercapacitor*

Metal oxides like RuO_2, MnO_2, V_2O_5, Fe_3O_4, Co_3O_4, NiO and TiO_2 exhibit excellent performance for supercapacitor devices. However, some of them suffer from low conductivity, poor stability and poor rate capability. To surpass these limits, the composites of metal oxides are prepared and applied. Some of them are summarized below.

3.2a *MnO_2-based composite*: MnO_2 composites with carbon-based materials like CNT and graphite have been reported earlier. Yan *et al* [7] developed MnO_2–CNT composite showing 115 to 950 F g^{-1} of capacitance, which is so far highest reported. They synthesized materials by reduction of potassium permanganate under microwave irradiation. CNT–MnO_2 composite electrodes with 1 M Na_2SO_4 aqueous solutions show 950 F g^{-1} of specific capacitance after 500 cycles. Graphene–MnO_2 composite also demonstrates high conductivity, high stability and large surface area. This composite exhibits 245 F g^{-1} of specific capacitance, which is 60% larger than prior to electroactivation. The MnO_2 nanoflowers coated on graphene show the specific capacitance of 328 F g^{-1} at 1 mA current rate with an energy density of 11.4 Wh kg^{-1} and 25.8 kW kg^{-1} of power density [7,8].

3.2b *RuO_2-based composite*: Ruthenium oxide (RuO_2) is one of the most promising materials for supercapacitors. It has many advantages, such as easy synthesis, high capacitance and fast cycling. Wang *et al* [9] have reported a 3D RuO_2 nanoparticles anchored to graphene and CNT hybrid foam nanocomposite system, which demonstrates superior gravimetric capacitance (502.78 F g^{-1}) and areal capacitance (1.11 F cm^{-1}). RuO_2 on graphene-coated copper foil is used as flexible electrode. RuO_2/Gr/Cu electrode with 0.5 M H_2SO_4 electrolyte exhibits a specific capacitance of 1561 F g^{-1} at a scan rate of 5 mV s^{-1} and a retention of 98% under the bent condition. The flexible RuO_2/Gr/Cu electrode exhibits a high energy density of ∼13 Wh kg^{-1} at a power density of ∼21 kW kg^{-1} [10].

3.2c *Fe_3O_4- and V_2O_5-based composite*: A nanocomposite with Fe_3O_4 nanocubes anchored on the surfaces of CNTs, was synthesized by hydrothermal method. It was observed that CNT as the supporting material could significantly improve the supercapacitor performance of the CNT/Fe_3O_4 nanocomposite. The resulting composite provides much higher specific capacitance of 117.2 F g^{-1} at 10 mA cm^{-2}, excellent cyclic stability and energy density of 16.2 Wh kg^{-1} [11]. The electrochemical performance of Fe_3O_4–rGO composite also shows remarkable results with specific capacitance of 220 F g^{-1} over 3000 charge/discharge cycles.

Following is the summary of a range of research activities undertaken globally:

- RuO_2 exhibited best performance with specific capacitance value of 1580 F g^{-1} and energy density of 39.28 Wh kg^{-1}.
- MnO_2 shows the specific capacitance of 1145 F g^{-1}.

Figure 3. (**a**) Aerogel carbon making machine. (**b**) Aerogel tape machine for making supercapacitor. (**c**) Aerogel supercapacitor developed by C-MET, Thrissur.

- Graphene alone can provide specific capacitance of 265 F g^{-1} and is a promising candidate.
- Ni–Co binary system shows excellent performance with 1846 F g^{-1} specific capacitance and energy density of 71.7 Wh kg^{-1}.
- In case of hybrid systems, CNT/PANI composite exhibited excellent performance with 314.6 F g^{-1} specific capacitance.

3.3 *Overview of supercapacitor work in India*

Recently, the micro-supercapacitors are promising as an energy device for energy sourcing in on-chip circuitry. However, a lower working electrode potential of the electrolyte e.g. <3 V and lower energy density limit the supercapacitor performance. Therefore, the fabrication of a micro-supercapacitor operating at highest voltage window of 8 V at ambient condition is one of the great achievement till date [12]. It could be achieved by designing micro-supercapacitors solid electrolyte-based nanofibres consist of supramolecular assembly of donor and acceptor molecules for carrying ionic charges using Ti electrode. These assembly structures provide an efficient channel for the fast diffusion of ions across the Ti electrodes surface offer the required stability at the ambient condition.

Misra and coworkers [13] proposed the micro-supercapacitor based on layer by layer coating of carbon nanotubes coated with manganese dioxide nanoparticles and MnO_2 nanosheets decorated with reduced graphene for diffusion of electrolyte in the electrodes. In this case, the ultra-high capacitance and energy density are observed to be 7.43 mF cm^{-2} and 0.66 μWh cm^{-2}, respectively. In current scenario, the miniaturized energy-storage device should be designed for enabling continuous and autonomous operation for its applications purpose [14,15]. Therefore, this is possible through use of nanostructured electrode material for designing the micro-supercapacitor. The progress in development of efficient miniaturized energy storage device is at primary stage and many challenges remain to be conquering, considering final applications in different field. IIT Kharagpur scientists have developed a new nanocomposite material suitable for supercapacitor with 472 F g^{-1} of capacitance at 0.5 A g^{-1} current density and 95% retention over 1000 cycles. There are many small groups in IISC Bangalore, IIT Mumbai, Indore, BHU, CECRI Karaikudi, NCL Pune and IISER Pune. Most of the work done by these groups is at academic level. However, the Centre for Materials for Electronics Technology (C-MET) has demonstrated the supercapacitor work at pilot level using carbon aerogel. Production facilities for carbon aerogel (2–3 kg batch) of high surface area have been established at C-MET Thrissur laboratory. Process technology for aerogel carbon production and fabrication of electrodes for supercapacitors has been developed (figure 3). C-MET Thrissur scientists have developed complete indigenous technology for aerogel supercapacitors (0.47–50 F) for various end applications through R&D support from DST, MeitY and BRNS. More significantly, indigenous aerogel-based supercapacitors have passed rigorous quality testing performed by several industrial end users and also demonstrated few applications with prototype. At present, the technology is ready for transfer with C-MET.

4. Batteries

The world demand for batteries is growing rapidly, especially in portable electronics. Batteries store energy in the form of chemical energy and are classified by chemistry used. By using this principle, subsequent types of batteries are developed:

Lead acid batteries: Lead acid batteries are robust, economical and tolerant to abuse. They consist of a lead-dioxide (cathode), a lead metal (anode) and a sulphuric acid solution (electrolyte). They are still in huge demand for automotive, stationary batteries for power backup, deep cycled batteries, etc. [16,17]. However, they usually limited by heavy size, short cycle life and less utilizable power. In addition to this, metals like lead are highly toxic and hence, appropriate disposal of lead acid batteries is needed [18,19].

Nickel-electrode batteries**:** Nickel-based batteries offer various advantages over lead acid batteries. There are several types of nickel-electrode batteries, such as nickel–cadmium (NiCd), nickel–metal hydride (NiMH) and Nickel–hydrogen (NiH) batteries [20–22]. For many years, NiCd batteries preferred for portable devices, however, they are expensive and involve toxic metal element like cadmium. NiMH batteries provide higher specific energy than NiCd and are available in market in various sizes, although they suffer from memory effect that causes capacity loss. There are other nickel batteries like NiFe, NiZn, etc., which are also available and have been useful for few applications. They have certain advantages, such as long shelf life, low corrosion, least self-discharge and wide temperature performance.

Sodium–sulphur batteries**:** molten salt battery**:** The sodium–sulphur battery filled with liquid sodium and sulphur possesses higher energy density, efficiency and longer cycle life [23]. The battery can operate at higher operating temperatures of 300–350°C [24]. It has, however, highly corrosive nature due to the formation of sodium polysulphides during electrochemical reaction. These batteries are, therefore, restricted to the applications, where temperature constraint does not exist [25].

Sodium nickel chloride batteries: molten salt battery: Sodium beta aluminate (β - Al_2O_3) is primary material in molten salt sodium nickel chloride batteries. Johan Coetzer invented similar version of the battery in 1977, namely, ZEBRA (zero emission battery research activities), which is a high temperature battery and can operate nearly at a range of 270–350°C. The cathode of the battery has sodium chloride and nickel powder, where the solid electrolyte is made with sodium beta aluminate, produced from low cost materials like boehmite (aluminium hydroxide). The solid electrolyte, a ceramic material, has the ability to conduct sodium ions. The sodium of the sodium chloride, therefore, passes through the solid electrolyte inside the battery, when a sodium film is formed on the surface of the electrolyte in the cell case [26]. The sodium diffuses back through the electrolyte in the discharge mode of the battery [27]. The maintenance of these batteries is nominal and does not have common degradation issues.

Zinc–bromine batteries: flow battery: Zinc–bromine battery (also known as hybrid redox flow battery) uses zinc metal-plated anode to store energy in the electrochemical stack during charging [28–30]. Total energy storage capacity of the battery thus, depends on electrode area and electrolyte storage reservoirs, which consist of two different electrolytes, microporous polyolefin membrane sandwiched between two compartments of flow past carbon–plastic composite electrodes. The cathode side contains an organic amine compound-based electrolyte, whereas the anode side contains purely water-based electrolyte [31]. These batteries are suitable for defense application.

Polysulphide–bromide batteries: flow battery: The sodium bromide and sodium polysulphide salt solution are used as electrolytes in polysulphide–bromide battery [32–34]. Sodium ions maintain the electroneutrality of the cell. Technology is environmentally sound; however, the toxic bromine vapour leakage is a concern. Sodium bromide serves as electrolyte on cathode side, whereas sodium polysulphide is used on anode side. The battery is promising as the starting material of this battery are abundant. The cell operating temperature is typically between 20 and 40°C [35].

Vanadium redox batteries: flow battery: Technology of vanadium redox flow batteries uses existence of four different oxidation states of vanadium [36]. This redox flow battery has only one electroactive element instead of two. Presence of same element in both half-cells reduces the chances of contamination and enhanced the lifetime of the electrolyte significantly [37,38].

Lithium-ion batteries: secondary battery: The nickel–cadmium is the most suitable battery for portable equipments including wireless communications to mobile computing. Lithium ion batteries (LIBs) have established as the most promising battery chemistry due to the following:

- Its energy density is higher than that of the standard nickel–cadmium. The battery pack designs with only one cell can have high cell voltage of 3.6 V, which is suitable for mobile phones. A nickel-based pack requires three 1.2-V cells connected in series.
- Relatively low self-discharge, which is less than half of that of nickel-based batteries.
- The maintenance of this battery is low compared to most other chemistries. No memory and scheduled cycling are required to prolong the battery's life.
- Lithium polymer batteries are of lightweight and flexible forms with improved safety.
- LIB has, however, few drawbacks like fragility, also requires a protection circuit to maintain safe operation, and temperature requires monitoring. Ageing is a concern with most LIBs.

Researchers are actively engaged to overcome these limitations of LIBs and make them more economic and sustainable.

4.1 *LIBs*

The first commercialized LIB was introduced by SONY in 1991. This revolution has changed the world in defining the technology for portability and mobility, specially for most personal electronics and electric cars [39]. The consumer products are estimated to use the LIBs with a total storage capacity of about 45 gigawatt-hours (GWh). The production of LIBs for electric vehicles has already reached 25 GWh in 2016 [40]. The growing demand of LIBs requires advancement of its components, such as anode, cathode, electrolyte, separator and current collector. Advancement on active materials focusses at higher energy density without increasing the cost.

4.2 *Global R&D trends in LIBs*

Extensive research on the cathode and anode materials of the LIBs as well as their electrolytes, separator and current collector are the priority among the academicians and to improve the performance of LIBs. In the following section, recent progress in the field of LIB materials is discussed in detail.

4.2a ***Cathode materials***: Li-based cathode materials are considered to be most promising for LIBs. LCO ($LiCoO_2$) is the most popular cathode material in commercialized LIBs. Alternatives to LCO have, however, been developed by researchers to improve existing energy density and charging–discharging characteristics. Some of these chemistries have already been introduced into the market.

***Layered lithium transition metal oxides*:** The layered lithium transition metal oxides have already been commercialized for LIBs. In this technology, $LiMO_2$, where M = Co, Mn and Ni or a combination of these metals are used. Layered structure facilitates diffusion paths for lithium ions. $LiCoO_2$ is the most extensively studied cathode material among these structures. The discharge capacity achieved so far is very low (~135–150 mAh g^{-1}), though its high theoretical capacity reported as 274 mAh g^{-1}. Enhancement of its capacity and ionic conductivity have been attempted through carbon coatings with oxide compounds [41], the cation doping, however, affects the overall capacity of cathode materials [42,43].

$LiMnO_2$ is superior due to its safety features as well as having low cost. It, however, has challenges on mass production, low capacity and power charge/discharge performance, especially, at high temperatures [44]. Nickel has higher energy density than cobalt. $LiNiO_2$ shows similar charge–discharge characteristics, and that of $LiCoO_2$, however, poor solubility in organic electrolyte solutions is the challenge. $LiNiO_2$ synthesis and treatment often require harsh temperature conditions [45]. Layered derivative compounds including $LiNi_xCo_{1-x}O_2$, $LiCo_xM_{1-x}O_2$, $LiNi_xM_xO_2$ and $LiNi_xM_yCo_{1-x-y}O_2$ (where M = Al or Mn) have also been attempted to improve the cycling performance. Starting from porous MnO_2 microspheres, hollow microspheres assembled with $0.3Li_2MnO_3 \cdot 0.7LiNi_{0.5}Mn_{0.5}O_2$ nanocrystals were developed [46] to exhibit a highly reversible capacity of about 295 mAh g^{-1} over 100 cycles and excellent rate capability as a cathode in Li cells. Several coatings on numerous Nickel-rich $Li(Ni_xCo_yMn_z)O_2$, layered structure materials (NCM, $x > 0.5$, $x + y + z = 1$) (e.g. ZrO_2 [47], TiO_2 [48,49], SiO_2 [50]) have been studied to establish the improvement in cycle stability of the investigated active material when used in low amounts.

***Spinel lithium transition metal oxides*:** The spinel lithium manganese oxide, $LiMn_2O_4$ is considered as an eco-friendly, non-toxic and low-cost material, having practical discharge capacity of 100–120 mAh g^{-1} (theoretical capacity of 148 mAh g^{-1}) [51]. Manganese-substituted spinels of the structural formula $LiM_xMn_{2-x}O_4$ (M = Co, Cu, Al, B, Cr, Fe, Ga, Ni, Ge, Na, Ti, Sc or Zn) had been studied to improve the cycling performance of $LiMn_2O_4$ [52–54]. Higher reversible capacity of $LiNi_{0.05}Mn_{1.95}O_4$ electrode prepared by sol–gel method was also reported [55]. Improvement of electrochemical performance had been reported by modification of surface, dispersion of $LiMn_2O_4$ nanoparticles in CNT [56–58]. Similar study had also carried out with other derivatives including $LiNi_xMn_{2-x}O_4$ and $LiCr_xMn_{2-x}O_4$ [59,60]. Olivine-structured compounds, lithium transition metal phosphates and silicates ($LiMPO_4$ and $LiMSiO_4$), found to hold a long voltage platform and their structure does not change during lithium intercalation and deintercalation. $LiFePO_4$ is becoming popular due to its low-cost, non-toxicity and better stability. It, however, lacks in electronic conductivity and low electrochemical performance at room temperature [61]. Improvement in material processing techniques, including solid solution doping in metals and carbon coatings on phosphate particles could overcome these drawbacks [62,63]. Poly-anionic compounds, silicates, including Li_2MnSiO_4 [64], Li_2CoSiO_4 [65], Li_2FeSiO_4 [66] and $LiFeSO_4F$ [67] have also been extensively studied.

***Nanostructured metal oxides and composites*:** It is reported that the vanadium-based oxides (VO) like V_2O_5 had good electronic conductivity, high energy density and superior chemical stability in polymeric electrolytes [68]. Vanadium exists in various oxidation states from 2+ in VO to 5+ in V_2O_5, which offer a wide range of capacities as cathode materials [69]. Series of vanadium oxides, including V_2O_5, LiV_3O_8 and $Li_3V_2(PO_4)_3$ had been investigated and found to have promising electrochemical behaviour. Layered compound V_2O_5 is having high theoretical capacity of 442 mAh g^{-1}. It is, however, having low ionic conductivity and poor cyclability due to microstructural failure upon cycling. Electrochemical performance can be improved by structural and composition optimizations [70]. Varied conductive polymeric materials, including polypyrrole [71], poly(ethylene glycol) [68], polyphosphazene [72] and polyaniline [73] had been attempted as hybrid hosts of V_2O_5 to improve thermal stability. On the other hand, LiV_3O_8 had shown promising electrochemical properties [74]. It was reported that synthetic routes affect the capacity of LiV_3O_8 cathodes.

4.2b ***Advanced cathode materials***: Organic electrodes were becoming popular due to its abundant, flexible, non-toxic, cost-effective nature. Their limitations, however, were cycle life, thermal stability, low energy density values and rate capability. A high-energy organic cathode material; poly(2,2,6,6-tetramethyl-1-piperidinyloxy-4-yl methacrylate)

(PTMA) had been attempted to obtain good power capability, cycling efficiency, fast charging and discharging, and can transfer specific capacity over 100 mAh g^{-1} [75].

The lithium-air batteries are developed with organosulphur materials [76,77]. The sulphur element is considered as the cheapest cathode material for lithium batteries with highest theoretical capacity density of 1672 mA g^{-1} [78]. Sulphur has, however, the dissolution of its reaction product polysulphides into the electrolytes and highly insulating nature, which discourages to use sulphur directly at low temperature as an electrode material for lithium batteries. This application would cause various challenges, such as rapid fall of the capacity and short utilization of active material [79]. Different fluorine-doped intercalation cathodes are also produced as cathode materials.

4.2c ***Anode materials***: The choice of suitable anode materials would be crucial to improve the energy and power density of LIBs. The carbon- and non-carbon-based materials had been extensively attempted for the development of advanced anode electrodes for LIBs.

Insertion/de-insertion materials: Carbon-based anode materials for LIBs have been used due to their availability, stability and electrochemical reversibility. Soft carbon (graphitizable carbon) is commonly used as anodic carbon materials in LIBs with reversible capacity of 350–370 mAh g^{-1}, long cycling life and good coulombic efficiency [80–83]. The graphite, however, suffers from low specific capacity. Researchers are, therefore, attempting on porous carbon, carbon nanotubes (CNTs), nanofibres and graphene. It is observed that the size and shape of these carbon-based materials improve the energy storage capacity. Hard carbon (non-graphitizable carbon), on the other hand, is having high reversible capacity (>500 mAh g^{-1}) in the potential range of 0–1.5 V. The materials, however, suffer from low initial coulombic efficiency and low tap density, which affects cycle life [84].

Among carbon-based active materials, CNTs show highest capacity of 1116 mAh g^{-1}. The coulombic efficiency of CNTs is affected due to the presence of large structure defects and high voltage hysteresis effect, which can be overcome by modifying morphological features of CNTs, like wall thickness, tube diameter, porosity and shape [85,86]. CNTs combined with a variety of nanostructured materials (Si, Ge, Sn, Sb) or metal oxides (M_xO_y; $M_{1/4}$Fe, Mn, Ni, Mo, Cu, Cr) could be useful to improve the lithium storage capacity and the cycling life in batteries [87–91]. Such hybrid systems enhance conductivity and reduce volume expansion in CNTs during the charging and discharging processes. Graphite with few graphene layers had been studied to improve surface and reversible capacity [92]. *In situ* fabrication of doped hierarchically porous graphene electrodes had been attempted for ultrafast and long cycling capability of LIBs [93].

Titanium-based oxides had been shown suitability in designing the operational devices with minor safety concerns. The materials were also inexpensive, low toxic, an excellent cycling life and with low volume change (2–3%) on both lithium insertion and de-insertion [94–97]. The host, however, suffers from low theoretical capacity and low electronic conductivity. Spinel $Li_4Ti_5O_{12}$ is most appropriate titanium-based oxide material for their excellent Li-ion reversibility at the high operating potential. Its structure and the spinel symmetry remain unaltered during the insertion process [92,98]. Moreover, TiO_2 is known for high electroactivity, strong oxidation capability, good chemical stability, high abundance and structural diversity [94,99]. Titaniaum is, therefore, considered as a good anode material in LIBs, especially for hybrid electric vehicle (HEV) applications. The lithium intercalation/de-intercalation process in titanium would depend on its crystallinity, particle size, structure and surface area [100].

The alloy/de-alloy materials including silicon, silicon monoxide, germanium and tin oxide are promising alternatives and can provide high capacity [101,102]. Major challenge is the change in volume during cycling, which can overcome by making nanoscale particles and composites. Silicon, among these, has highest gravimetric and volumetric capacities [103,104]. Silicon is also second most abundant element on earth, eco-friendly, cost effective and show discharge potential near to graphite. SiO is also considered as an anode candidate, because of its high theoretical capacity of >1600 mAh g^{-1}. Germanium and its composites, SnO_2, MoS_2 are used as active anode materials for LIB.

Conversion materials: The transition metal compounds like sulphides, oxides, phosphides and nitrides (M_xN_y; $M_{1/4}$Fe, Co, Cu, Mn, Ni and $N_{1/4}$O, P, S and N) can be used as anode materials in LIBs. Transition metals carry out redox reactions. Anodes based on these transition metals exhibit high reversible capacities [105].

4.2d ***Electrolytes***: An electrolyte, an inert component in the battery, should demonstrate stability against both electrodes. Good ionic conductivity, electronic insulation, wide electrochemical window, chemical and thermal stabilities are the desired properties.

Non-aqueous electrolytes

Commercially used electrolytes for LIBs are non-aqueous solutions, in which lithium salts like lithium hexafluorophosphate ($LiPF_6$) are dissolved in organic carbonate solvents, specifically, propylene carbonate (PC), ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC), independently or in combination. However, these solvents are volatile and highly flammable, hence it is highly needed to replace them by safer electrolytes. Zhang *et al* [106] introduced organic fluorocompounds, which have superior electrochemical properties compared to commercially used EC/EMC-based electrolyte. Organic carbonates are known to create solid electrolyte interphase (SEI) on electrode surface, which acts as a protecting layer between electrodes and electrolyte.

Ionic liquid (IL) electrolytes: Ionic liquids are non-volatile and non-flammable in nature. They exhibit specific characteristics, such as high conductivity, wide electrochemical stability window, thermal and electrochemical stabilities and good solubility of various compounds. With these properties, they can be excellent alternatives to organic-based solvents. However, they suffer from high viscosity and high cost. There are many types of cations like imidazolium and pyrrolidinium and anions are available with which number of ionic liquids can be designed [107].

Polymer and glass/ceramic-based electrolytes: The solid state batteries are the next breakthrough in LIBs. These batteries need solid state electrolytes to prepare complete solid batteries. Polymer-based electrolytes are attractive for solid state batteries as they show ionic conductivity safer than liquids and as they are in the form of films no extra separator is needed. They could be classified as solid polymer electrolytes and gel polymer electrolytes. Toyota's Research group has reported $Li_{10}GeP_2S_{12}$ (LGPS) as a new solid electrolyte, which has a 3D framework structure and ionic conductivity of 12 mS cm^{-1} [108]. The 3D ion-conducting network based on percolative garnet-type $Li_{6.4}La_3Zr_2Al_{0.2}O_{12}$ nanofibres, not only increase the ionic conductivity, but also mechanical strength of the polymer electrolyte [109]. DeSimone *et al* [110,111] developed perfluoropolyethers (PFPEs)-based polymer electrolyte showing high conductivity and high thermal and electrochemical stabilities. Many research groups reported copolymers and glass-polymer composites that transport lithium ions in LIBs [112–114].

Researchers investigated Li_2S–P_2S_5-based solid electrolyte [115]. The combination of a lithium-halide-based solid electrolyte with lithium metal can prevent the growth of dendrites. Iodine-enhanced electrolyte may propose a 'self-healing' process that protects the electrode from dendrites [116]. Fluorinated solvents with additives exhibit stability up to 4.55 V. Many additives such as vinylene carbonate, cyclohexylbenzene, pentafluoro(phenoxy)cyclotriphosphazene [117–122] have been reported to improve the performance of LIBs.

4.2e ***FLIBs***: Flexible lithium ion batteries (FLIBs) are the next generation LIBs. FLIBs require both flexible electrodes and flexible electrolytes. Solid electrolytes used in FLIBs act as both separator and electrolyte. Thin polymeric materials are usually used for FLIBs packaging materials. Globally, a lot of research work is going on to develop high performance FLIBs.

Recent development in the FLIBs:

- A novel cable-type LIB was introduced by Kwon *et al* [123] by using a hollow spiral Ni–Sn anode with a multi-helix structure, a modified polyethylene terephthalate nonwoven separator, and a LCO cathode coated on an aluminium wire. Though the concept is promising, it suffers from capacity fading due to unstable Sn-based anode material. Lee *et al* [124] replaced Ni/Sn alloy anode by a conventional graphite anode material, which improved capacity retention of 90% after 45 cycles.
- Wire-shaped micro-batteries were designed by Peng and coworkers [125] using aligned CNT fibres wound around a lithium wire and PVDF separator. These structures ensure their use in electronics textile, but shown low rate capability for batteries. Yu and coworkers [126] demonstrated tantalum trisulphide (TaS_3) nanowires as a new self-supported and flexible anode material for Li-ion batteries with high specific capacity 400 mAh g^{-1} and excellent electrochemical cycling. Nevertheless, there are very few materials that have been explored recently, especially, metal oxides [127], some metal nitrides [128,129], sulphides [130] and alloy materials [131].

Yang *et al* [132] developed a microfluidic-assisted technique to pattern a grid-like transparent anode ($Li_4Ti_5O_{12}$)/cathode ($LiMn_2O_4$) on a flexible polydimethylsiloxane (PDMS) substrate for transparent electronics. However, it needs improvement to increase the energy density. Lately Koo *et al* [133] exhibited a bendable FLIB using mica substrates. Stretchable batteries with biaxial stretch ability by using a segmented design in the active materials have been reported [134].

4.3 *Overview of LIB work in India*

India is one of the largest markets for portable LIBs. Hence, much advanced materials are needed to develop improved LIBs. Regardless of significant advances in LIBs during past decades, it still requires a number of techniques and materials to complete ever growing demand. In India, few groups like IIT, Mumbai and IISc, Bangalore are developing solid-state electrolytes and electrodes for batteries, which is too at academic level. Development of in-house full functional LIB with both electrode and electrolyte materials is still missing. The efforts are minuscule in this direction. Entire efforts are concentrated at academic level and hence, the development at the prototype levels i.e. full cell and the pilot stage production required to be emphasized.

However, C-MET has initiated research on battery material since 2000 in collaboration with France and Singapore. Earlier, the fabrication facility was not there and hence, the developed materials had been supplied for development and testing in battery in France and Singapore. C-MET established whole fabrication facility in 2016, by taking into account the growing demand of the indigenous technology for the country. The synthesis and scale-up of active materials for

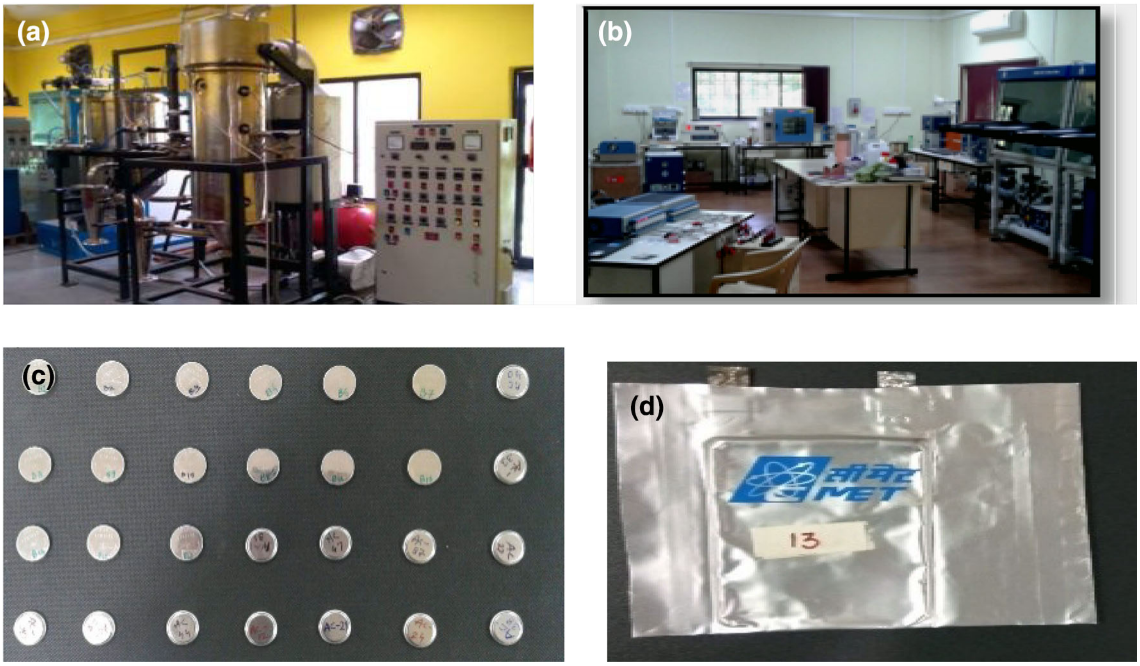

Figure 4. (**a**) Spray dryer for large scale synthesis of active materials. (b) Photograph of battery fabrication and testing facility developed at C-MET, Pune. (**c**) Prototype of coin/button. (**d**) Pouch cell fabricated using active materials developed by C-MET, Pune.

electrodes had been started. C-MET developed a full battery fabrication and testing provision for the button/coin type and pouch/rectangular cells under single roof. The development of materials for high energy batteries requires constant upgradation and improvement.

Research activities at C-MET include development of materials for the high capacity and energy density. The facility has already been developed for the large scale synthesis of active materials (500 g batch level) *via* spray dryer technique (figure 4). Active materials for anodes like lithium titanium oxide (LTO) and nanostructured spherical hard carbon from natural sources, such as potato, banana and sweet potatoes have been synthesized and optimized. This invention has been submitted for Indian patent. These developed materials were compared with the commercially available materials (such as Aldrich and MTI, Corporation USA make) and fabricated prototype button/coin (2032 type) cells. Figure 4 shows the battery fabrication and testing facility, coin/pouch cells developed at C-MET, Pune. The performances of these cells are found to be comparable to that of the commercially available active materials. C-MET, Pune has carried out subsequent activities using in-house facilities and also had training in South Korea on flexible batteries:

- **Lithium air and sulphur batteries:** These are the upcoming types of batteries and C-MET has designed and developed materials for such batteries. Also, a freshly designed glove box has been dedicated for materials processing and battery fabrication. C-MET has collaborated with Korea and UK for these batteries. These materials are estimated to furnish high capacity.
- **Na-ion battery:** Easy availability of sodium metal reduces the cost of Na-ion battery compared to Li-ion battery. C-MET has taken initiative to develop materials and fabrication of the Na-ion batteries. Few materials, such as $NaFePO_4$ and $NaCoO_2$ have been developed and fabricated few cells. These types of batteries will be promising for e-vehicles.
- **Flexible Li-ion batteries:** Globally electronics market is slowly moving towards miniaturization of electronic devices. There is a huge market for flexible electronic devices. The wearable electronics is already in market. Ultimately batteries need to be miniaturized and flexible to make them compatible with approaching advanced electronic devices. It is established that the nanostructured materials play significant role to develop such batteries. C-MET is pioneer in the development of nanostructured materials for different electronic applications and now has started producing materials for batteries too. Currently, solid polymer electrolyte using biomass has been developed and reported in 'ACS Applied Materials and Interfaces' journal [135].
- **Glass solid electrolyte:** C-MET has expertise and facilities for creating diverse types of glasses for both optical and energy applications. The glass electrolyte for Li-ion battery is also been pursued actively. The developed ionic glass has been carried out many trials in laboratory stage for actual use in battery fabrications.

Table 2. Global manufacturers of supercapacitors.

Name of the companies	Specialities	Location
Skeleton Technologies	High power densities, EDLC type symmetric supercapacitors	Estonia
Maxwell Technologies Market leader, worldwide presence	EDLC type supercapacitors, automotive engine starting, kinetic energy recuperation systems (KERS), torque augmentation, wind turbine, Maxwell supercapacitors are not known for highest energy density or power density, but most cost-competitive, considering the benchmark of the 3000 F, these supercapacitors are 30% cheaper than the closest competitor in the automotive segment, Ioxus	USA
C2c New Cap	Nickel–carbon hybrid supercapacitor with aqueous electrolyte. 1.2 volts	Portugal
The Paper Battery Company	Hybrid supercapacitors	USA
Angstron Materials	Graphene-based EDLC supercapacitors	USA
Ioxus Close competitor to Maxwell with worldwide presence.	Very high power density supercapacitors with organic electrolytes. Transportation mainly hybrid buses, wind turbines, grid power conditioning, industrial forklifts. Fully vertically integrated, from development, electrode, cell and module manufacturing to commercialization. Their supercapacitors are designed from the application perspective rather than pursuing the highest energy and power density possible	USA
Cap-XX	Consumer electronics, wireless networks, RFID. Development focus is on supercapacitor modules and control circuit suitable for use in the automobile industry, such as stop–start system and regenerative braking systems. Focus is also on enhancement of performance of the existing line small supercapacitors	USA
Nesscap	Consumer, industrial, automotive. Nesscap is integrated vertically from manufacturing of electrodes, cell and module assembly and commercialization of supercapacitors	Korea
Cooper Bussmann	Transportation, buses, trains, trolleys, commercial trucks, heavy equipment (mining, construction, cranes). Company started with carbon aerogel supercapacitor, having very low ESR and high specific capacitance. Company has also used activated carbon as the electrode material	USA
WIMA	Power electronics, automotive, railway technology, wind power system, UPS WIMA supercapacitors works reliably under the hardest conditions. Its metallic rectangular case is tightly sealed by laser welding and therefore, defies the most severe temperature fluctuations	Germany
Nanotune Technologies	Electric vehicles, consumer electronics NanoTune's electrodes offer 20 Wh kg^{-1} energy density, which is significantly higher than current supercapacitor baseline (5 Wh kg^{-1} energy and 10 kW kg^{-1} power densities). Company offers graphene electrode supercapacitors	USA
NEC Tokin	Automobile engine start-up assist, regenerative braking Company competes only in small supercapacitors in the range of 20–70 F. Company uses non-flammable, non-toxic aqueous electrolytes and researching ionic liquids	Japan
Skeleton Technologies	Transportation (KERS and start–stop systems in hybrid vehicles), industrial, renewable energy, defense and space Products have four times higher power density (80 Wh l^{-1}), and almost double the energy density (14 Wh l^{-1}) compared to current industry standards. In a market dominated by US and East-Asian competitors, such as Maxwell Chemi-Con, Skelton Technologies plans to focus on sales and market with an emphasis on Germany	Estonia

Table 2. (continued)

Name of the companies	Specialities	Location
Yunasko	Transport (KERS and start–stop systems in hybrid vehicles); industry (cranes, forklifts, welding machines); energy supply and alternative energy (power grids, UPS, wind-mills, etc.); consumer tools, flash lights, etc. Yunasko develops both supercapacitors (they call them carbon/carbon ultracapacitors) and they have a new development, a supercapabattery (they call them hybrid ultracapacitor). Yunasko posseses world-best specific characteristics in terms of power and energy densities	UK

Table 3. Global manufacturing industries of LIB.

Name of the companies	Specialities	Location
Contemporary Amperex Technology Co. Ltd.	Transport, electric mobility Capacity: 12 GWh	China
Panasonic	Transport, electric mobility Capacity: 10 GWh	Japan
BYD Company Ltd.	Transport, electric mobility Capacity: 7.2 GWh	China
Optimum Nano Energy Co. Ltd.	Transport, electric mobility Capacity: 5.5 GWh	China
LG Chem	Transport, electric mobility Capacity: 4.5 GWh	South Korea
Tesla	Produced e-vehicles, building gigafactory in joint venture with Panasonic with annual battery production capacity of 35 GWh	USA
Samsung	Manufactures batteries for BMW and Volkswagen electric cars and plug-in hybrids	South Korea
Wanxiang	High power polymer LIB, integration motor as well as drive-control system, whole vehicle electronic/control system	China
GS Yuasa	Joint ventures with Mitsubishi Motors and Mitsubishi Corp.; provides batteries for Mitsubishi	USA
Lishen	Total energy solutions, including six product categories: cylindrical battery, prismatic battery, power battery, polymer battery, photovoltaic, ultra-capacitor and near thousand models, whose applications covering a wide range of customer electronics, new energy transportation and energy storage systems	China

5. Global market of energy storage systems

The market for energy storage systems around the world varies widely, particularly, in emerging economies with the development in industries. Every market requires precise applications of storage systems and types of technologies well-matched to local requisite, which further depends on various issues including mixture of existing generation resources and penetration of renewable, extent of the electricity market, electricity rate structures for customers, stability and reliability of the electricity grid with requisite frequency, etc.

Most activity in the energy storage market is happening in selected developed countries, where energy markets have favourable regulatory frameworks for extracting worth for storage projects. The success in energy storage market would oblige financial support to the ESS project development, which in turn would demand established technology offering warranties and performance guaranties on their products. The energy storage market growth has, however, a number of barriers to overcome, including level of competition, regulation in energy markets, etc. Regardless of these barriers, it is anticipated that energy storage will take part in the development of numerous budding markets in the coming decade. The major manufacturers of super-capacitors and their application areas are provided in table 2. Table 3 shows the major manufacturers of the LIBs and their application areas.

5.1 *Energy storage systems market in India*

To fulfil the growing domestic demand, India has enhanced its hardware electronics manufacturing base. With substantial growth in electronics, especially in portable electronic products LIBs and supercapacitors are in significant demand

Table 4. Manufacturing industries of supercapacitors in India.

Name of the companies	Location
Tirupati Internationals	Delhi
Electronicon System Electric	Nashik, Maharastra
Saison Components and Solution	Delhi
MG Automation Technology	Nagpur, Maharastra
Santronic	Mumbai, Maharastra
Simwayon Power	Noida, UP
Nikhil Electrolytics	Bhiwani, Haryana
SPEL Technologies	Pune, Maharastra

Table 5. Manufacturing Iindustries of lithium ion batteries in India.

S. No.	Name of the companies
1	Samsung SDI Co. Ltd.
2	Panasonic India Pvt. Ltd.
3	LG Polymers India Pvt. Ltd.
4	Sony India Pvt. Ltd.
5	Coslight India Telecom Pvt. Ltd.
6	NEC India Pvt. Ltd.
7	ACME Cleantech Solutions Pvt. Ltd.
8	Amco Saft India Ltd.
9	Rajamane Telectric Pvt. Ltd.
10	Semyung India Enterprises (Pvt.) Ltd.

in India. Demand is higher specifically in the advanced applications such as electronic gadgets, high resolution camera flashes, toys, self-start for two-wheelers, electric vehicles (EVs)/HEVs, solar energy harvesting/storage modules, power supplies, etc. those in actual fact require fast charging/discharge and high power. The supercapacitors are preferred for automotive and energy storage sectors, especially for the use in EVs and HEVs. Table 4 describes market in India for supercapacitors (table 5).

India has rapidly enhanced mobile manufacturing units, nearly 118 units of mobile handsets manufacturing units and their parts/components have set up their operation since 2015. The production of mobile handsets has gone up from 60 million units valued at USD 2.9 billion in 2014–15 to 225 million units valued at USD 20.3 billion in 2017–18. LCD/ LED TVs production has increased from 8.7 million units in 2014–15 to 16 million units in 2017–18. The value of LED products made in India has risen from USD 334 million in 2014–15 to USD 1.5 billion in 2017–18. Supercapacitors are in high demand and would increase to USD 8.33 billion by 2025 with CAGR of 30% until 2025, among which the automobiles and energy sectors demand would be ~11 and ~30% of the total. Ministry of Electronics and Information Technology, Government of India had carried out a market survey through ELCINA, New Delhi in 2016. Based on 'Supercapacitor Market Landscape Study 2016', at present the demand for supercapacitors in country would be ~1280.66 million for a range of sectors.

According to a market study in India, LIB market is forecast to cross 6000 crore rupees by 2022, on account of growing adoption of cell phones, cameras, etc. coupled with escalating number of solar and wind energy projects and increasing electric vehicle manufacturing in the country. Moreover, with growing penetration of e-rickshaws as a public transport in India, demand for LIBs in the country is expected to raise at a fast speed through the next five years.

In many such electronic devices, LIBs are either in use already or will be replaced the existing conventional batteries by 2020.

6. Conclusions

India has emerged as one of the fastest growing economy with the GDP of average rate of 7% during last 5 years. This growth is fuelling the aspiration of nearly 500 million young citizens. India has become one of the fastest growing markets for electronics in the world. The demand for electronics is estimated to grow exponentially to USD 400 billion by 2023–24. The requirement of the portable electronic gadgets is also increasing with the arrival of new products and aspiring young generation. It is quite clear that with the promising field of electrification of transportation and miniaturization, much superior technologies would be obligatory for storage devices. Henceforth, the demand of supercapacitor and LIB would exponentially increase in the forthcoming decade. It is expected that energy storage opportunity in India will be between 70 and 200 GW by 2022. Consequently, there is a great prospect for highly developed storage technology research and indigenous manufacturing base in India for new entrants.

The desired market would need button cells for consumer electronics and pouch cells for mobile and laptops. It is known that world economy rides on automobile sector, and the Indian picture is no different. The automobile sector is shifting towards electric-based mobility, which requires highly efficient supercapacitors and LIBs. The combination of both these ESS can fulfil the requirement of energy and power density for portable electronics. The research demand on variety of materials (electrolytes/cathodes/anodes) would enhance both energy storage systems. The $LiCoO_2$, $LiNiMnCoO_2$, graphite and $Li_4Ti_5O_{12}$ are generally used for LIB fabrication, while carbon- and nanostructure-based materials are used for supercapacitors. C-MET has the capability of producing all these materials, which will definitely pay dividend in the long run on both economic and environment fronts as a contribution towards the national fuel security policies.

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