Review and Outlook on Advances in Energy Storage Materials for Electric Vehicles

Suman Sharma¹, Neha Janu², Baibhav Bishal¹

¹Department of Electrical Engineering, Swami Keshvanand Institute of Technology, Management & Gramothan, Jaipur-302017 (INDIA)

²Department of Computer Science & Engineering, Swami Keshvanand Institute of Technology, Management & Gramothan, Jaipur-302017 (INDIA)

Email:suman@skit.ac.in, neha123jaipur@gmail.com, baibhav.bishal@skit.ac.in Received 11.02.2021received in revised form 13.12.2021, accepted 18.01.2022

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Abstract-Burden of oil imports, rising pollution, and international commitments to combat global climate change are among key factors motivating India's recent policies to speed up the transition to emobility. This paper reviews on advancements in energy storage materials for electric vehicles. Research is needed on nano-sized materials to improve the performance of energy storage on synthesis, characterization and optimization of novel electrode materials. It highlights drivers, strategies, categorization, and measures for smart batteries towards sustainable development.

Keywords-Electric vehicle, Li-ion batteries, smart materials, Solar PV system, sustainability.

1. INTRODUCTION

Recent years Materials for Energy and Environment protection, Health Care and Water technology are one of hot topic of interest by worldwide researchers. Maintaining a sustainable environment and a healthy lifestyle, reducing the air pollution, waste management required for any smart city development [1]. Any materials used for EV Battery development must be recyclable in nature for ensuring sustainability. Classification of Materials is based on the Utility and based on physical property. Green renewable clean Energy technologies viz. Solar, Hydro, Batteries, Bioenergy, photo catalytic water splitting, wind, mechanical, nuclear and geothermal energy etc. are required to solve present Environmental problems and pave way for sustainable development. Energy Storage Technology/Renewable

Technology/Electrochemical Engineering is interdisciplinary in area of materials, Mechanical & Automobile, Chemical Engineering, EEE, Engineering and Management. Research is needed on search for novel materials, processing and various characterizations for future Energy storage and Electric vehicle applications.

In smart city context, Smart materials are required for green buildings: Thermal insulation, heating and cooling, materials for energy-saving lighting robot shuttles, motors, parts [2]. Further, smart materials involve Smart glass, transparent smart plastic, transparent, magnetic materials. Smart operations involve advanced flexible organic electronic materials for photovoltaic membranes, bio-plastics, and advanced polymers. Materials for resistive switching memory applications, sensor materials, advanced smart materials for 5G, 6G electronics. Smart materials are desired for smart grid, Electric Vehicles, Autonomous vehicles, and Smart charging EV chargers (V1G, V2G (uni or bi-directional vehicle to Grid), V2B, V2H.

Fig.1 illustrates the importance of dynamic Energy Storage from electric vehicles. There is synergy between renewable energy (solar PV) technology and energy storage. The intermittency and variability of renewable energy resources can be addressed through dynamic energy storage from electric vehicles. Capacity of solar energy has increased 8 times. In 4 years, statistically 2.63 GW to 22 GW from 2014 to 2018 in India. India is going to reach a mark of 227 GW of nonconventional energy.Fig.2 depicts different types of solar PV systems.



Fig.1: Drivers for e-mobility illustrating energy storage significance

Types of solar PV systems.

- i. Grid Tied or Direct PV System: power can be generated and utilized for day time only
- ii. Off Grid PV System
- iii. Grid/Hybrid or Grid-Interaction system with Energy Storage (Battery bank); technology is more expensive. Power generated by PV

panels is in DC so we need an inverter to convert DC in to AC.



Fig.2: Types of solar PV systems

General Motors and Ford are leaders in the field of artificial intelligence (AI) and well positioned to benefit from technical advances, according to GlobalData's research. Autonomous vehicles (AVs) also known as self-driving vehicles uses AI software, light detection and ranging (LIDAR), and RADAR sensing technology [3]. An AI and computer vision-based robotics platform approach is utilized to digitize& automate material flows and for making intelligent autonomous robots that can perform in the real world. Real-world robotics hard, not only because of the unique is combination of software and hardware required but because of thebad conditions they are likely to face.GM and Ford are among the companies best take advantage of future positioned to autonomous vehicles disruption in the automotive industry.Major benefits of AVs: lowering fuel consumption, reduce CO2 emission, and reduction in congestion. AVs will generate a \$ 7 trillion annual revenue stream by 2050. Widespread adoption of AVs could lead to a 90% reduction in vehicle crashes. Fig.3 illustrates early lithium-battery development.

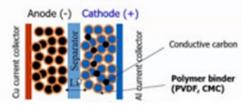


Fig..4 Early lithium-battery development

- Cathode=Positive electrode (LiCoO2, LiFePO4, LiMn2-xNixO4), Li is replaced by Na, K
- Anode=Negative electrode (Li, Na, K, Carbon, Si, SnCoCx, LTO,MO, Ca, Zn, Mg)
- ii. Charge=Oxidation=anodic scan; positive current, SOC (state of charge)
- iii. Discharge=Reduction=cathodic scan; negative current
- iv. Electrolytes: Liquid 1MLiPF6 (EC:DMC), Ionic liquids, Polymer and solid electrolytes
- v. Current collectors: Cu foil for anodes, Al foil for cathodes
- vi. Polymer Binder: PVDF, CMC, SBR; Conducting carbon: Super P carbon

Different lithium ion battery configurations and their attributes for specific applications are represented in Fig.4. Fig.5 demonstrates Electric vehicle: Tesla Model S with battery pack of capacity 85 kWh. Cell type: 18650 (NCA chemistry). Single cell capacity: 3.2 Ah. Number of cells: 7104. Battery weight: 540 Kg/1200 lb. Battery voltage: 375 V. EV batteries involve various life cycle processes as shown in Fig.5

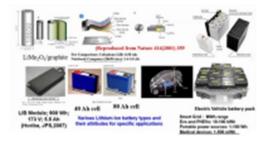


Fig. 4 Different Lithium ion Battery configurations and their attributes for specific applications [4]



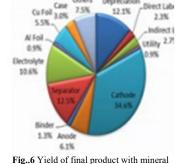
Fig. 5 Battery life cycle process

- i. Li, Ni, Mn, Co, Fe, P: Electrolyte, cathode
- ii. Graphite (Natural and Artificial): Anode
- iii. Cu, Al, Steel: Cell Manufacturing, Battery pack assembly
- iv. Nd: Neodynium, Dy: Dysprosium: Permanent magnet for electric motors

Fig.6 shows yield of final product with mineral as mentioned below:

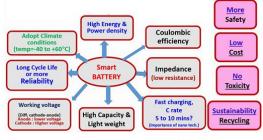
30 tons of mineral gives 30 Kg of Cobalt # 5 tons of mineral gives 60 Kg of Ni

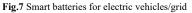
- #6 tons of mineral gives 40 Kg of Cu
- # 1 ton of mineral gives 90 Kg of Graphite



Any kind of battery must meet a range of performance criteria which vary in importance depending on application. Fig.7 shows attributes of smart battery to be employed in electric vehicles or smart grid applications.Fig.8 denotes

principle of operation for battery used in electric vehicle or grid. Fig.9 represents block diagram for the key components of battery electric vehicle as battery charger, battery, inverter, motor, DC-DC converter, and associated software and electronics. Further, Fig. 10 classifies motors employed in electric propulsion system.





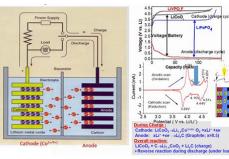


Fig. 8 Principle of operation of battery for electric vehicles/grid

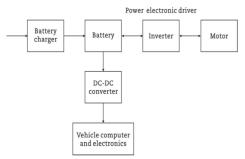


Fig. 9 Key Components of Battery Electric Vehicle

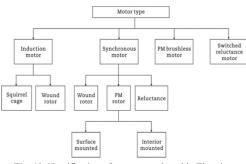


Fig. 10 Classification of motors employed in Electric Propulsion System

Fig.11 depicts schematic of advanced charging system of electric vehicles used in V1G/V2G technologies. Table I provides comparison of

different devices based on parameters viz. voltage drop, control power, control mode, switch speed, voltage rating, and cost. Table II compares the charging levels for EVs based on voltage rating, current rating, useful power, maximum output, charging time, and connector utilized.

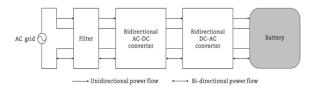


Fig.11 Schematic of advanced charging system

Table 1 Comparison of devices

Devices	IGBT	Transistor	Mosfet
Voltage drop	Medium	Low	High
Control power	Low	High	Low
Control mode	Voltage	Current	Voltage
Switch speed	Fast	Medium	Very fast
Voltage rating	Medium	Medium	Low
Cost	Low	Low	High

Table 2 Comparison of Charging Levels for EVs

Quantity	Level 1	Level 2	Level 3
Voltage (V)	120	208/240	200-450
Current (A)	15	40	125
Useful power (kW)	1.4	7.2	50
Maximum output (kW)	1.9	19.2	150
Charging time (h)	12.00	3.00	0.33
Connector	J1772	J1772	J1772 combo

Table 3 differentiates the types of lithium-ion cells and energy density. Tables IV and V illustrates comparative analysis of primary and secondary batteries respectively, based on anode and cathode material used, electrolyte/reaction involved, nominal voltage/current, and associated practical capacity.

Table 3 Comparison study of Lithium-ion Cell

Cell type	The energy density per weight	The energy density per volume
LTO	90	200
LFP	130	247
NMC	150	300
NCA	240	670

3. CAPACITY EVALUATION, ENERGY AND POWER DENSITY

Fig.12 shows useful parameters to evaluate capacity, energy density, and power density. Fig. 13 displays voltage of cell at constant current. An ideal anode material must show lower operating voltage, and cathode must show high operating voltage. LiPO4F cathode has higher Energy density.

Voltage of cell= $E_{cathode}$ - E_{anode}

Capacity= Time*current/(weight of active material in g)

Energy density of Lithium-ion Batteries

Specific energy or energy density = [Battery nominal voltage (V) X Battery capacity rating (Ah)/battery weight]

For example, for a 18650 cell, nominal voltage, 3.6 V, capacity rating 3.0 Ah, cell weight, 45 g, then the energy density will be roughly 240 Wh/kg.

Lithium-ion Batteries:

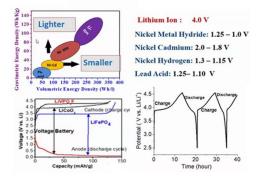


Fig.12 Useful for capacity evaluation, Energy and power density

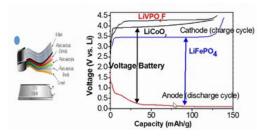


Fig. 13 Voltage as a function of time at constant current [10]

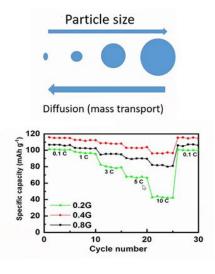
Power density:

The formula for power is P(W) = VXI. As an example, if nominal (average) voltage is 3V and 1A current the power is 3W then this value can be divided by liter or kg to find the power density.

Experimental Capacity = Step time*Current/(3600*Mass of active material)

Theoretical Capacity = (26800*n/M) mAh/g Where, n = number of moles of Li+ ions reacted (for FeO, n=2); F= Faraday's constant, and M= molecular weight of the compound Capacity fading = discharging or charging Capacity (2nd-nth(50)/2nd cycle)*100 Coulombic efficiency = (discharge – charge capacity)=x=97-99 percent efficient is good Due to mass transfer kinetic limitations, higher current rate is expected to lower capacity. V=IR, I=V/R

Fig.14 illustrates C-rate of battery [5]. C-rate is calculated using current density- Current/mass. 1C= total energy stored is delivered in 1 hr. 0.1C (C/10)=total energy is delivered in 10 hr. 5C= total energy is delivered in 12 min



1. MEASURES ADOPTED TO IMPROVE RATE CAPABILITY OF ELECTRIC VEHICLES APPLICATIONS

Measures adopted to improve rate capability of Electric vehicles applications are nano size, porous materials design, improve electronic conductivity of electrode of cathode and anodes material, electrode design, current collector modifications, appropriate electrode thickness [6,9]. Impedance values are sensitive to discharge/charge voltage and cycle number and type reaction mechanisms (intercalation/alloying and conversion reactions).Fig.15 represents safety ensuring strategies in Li-ion batteries. The environmental impacts arising from spent LiBs include ecotoxity, resource depletion, global warming, and human health impacts. For ex: chemicals, when discharged, percolate into the ground leading to ecotoxity and water pollution in the ecosystems. Electrolyte reacts with H2O leads to HF. Thus, LiBs cannot be disposed of anyhow and require a proper waste disposal system. Li-ion Battery recycling by (a) Direct (b) Hydro Process and (c) Pyroprocess Recycling, Pyrometallurgy and Hydrometallurgy combination of both techniques. Fig. or 16 illustrates measures for sustainability. Figs. 17-19 summarizes respectively EVs, ESS for EVs and BEV manufacturing [7].

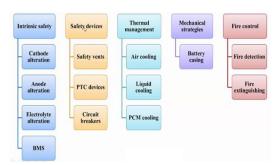


Fig. 15 Strategies to ensure safety in Li-ion batteries



Fig. 16 Greener LiBs of organic electrodes derived from biomass for sustainability

2. CONCLUSION

Efforts are being made on nano/submicron sized materials to improve the performance of energy storage through extensive research on synthesis, characterization and optimization of novel electrode materials. Among all cathodes LiNixMnyCozO2-811,22, LiFePO4, LiMnxNiyO4 and Graphite, Li metal, Li4Ti5O12 (LTO), Si/Carbon, Carbon: SnCox composites are used in commercial electric vehicles. Nice scope for novel Nano composite materials and large scale synthesis (zero liquid discharge, greener synthesis) of electrode and electrolytes for batteries and materials recovery and sustainability. Cheaper, safe, long-life performing novel green materials is likely to come up. Research on high ionic conductivity polymers are needed to operate at RT. Cooperation between scientists and engineers, which could facilitate the fabrication of large-area Energy systems and address the current clean transportation technology challenges.

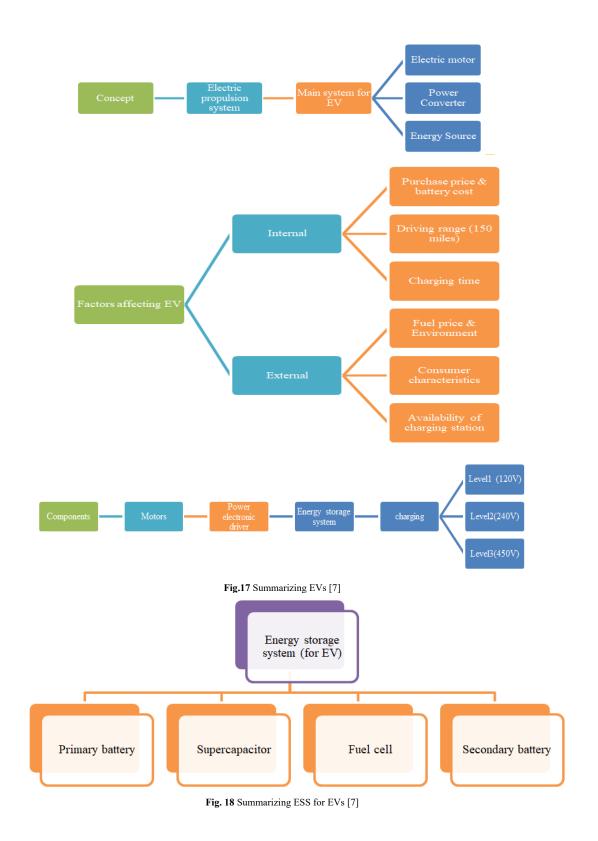
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Primary battery	Cathode material	Anode materia l	Electrolyte/reaction	Nominal voltage/curr ent	Practical capacity
Zinc-carbon and alkaline manganese	MnO ₂	Zn	Aqueous KOH/NH4Cl $Zn + 2MnO_2 + 2H_2O \rightarrow 2MnOOH + Zn(OH)_2$ $Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3$	0.16-44A	75-35 A-h/Kg
Zinc-air	O ₂	Zn	Alkaline electrolyte $Zn + 2OH \rightarrow Zn (OH)_2 + 2e^{-} (anode)$ $O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} (cathode)$ $Zn + (1/2) O_2 \rightarrow ZnO (uverall reaction)$	0.4-2mA	40-600 mA-h
Silver-oxide	Zn	Ag ₂ O	KOH or NaOH aqueous electrolyte Zn + Ag2O \rightarrow ZnO +2Ag (overall reaction)	1.5-1.6 V	165 mA-h
Lithium-sulfur dioxide	Teflon- bonded acetylene black	Li	$2Li + 2SO_2 \rightarrow Li_2S_2O_4$ (overall reaction)	2.7-2.9 V	-260 W-h/Kg
Lithium-thionyl chloride	Porous carbon	Li	$4Li + 2SOCl_2 \rightarrow 4LiCl + S + SO_2$		450-600 W-h/Kg
Lithium- manganese dioxide	MnO ₂	Li	Ion conducting organics $Li \rightarrow Li^+ + e^-$ (anode) $2MnO_2 + Li^+ + e^- \rightarrow MnO_2$ (Li ⁺) (cathode) $MnO_2 + Li \rightarrow MnO_2$ (Li ⁺) (overall reaction)	3.60 V	200 W-h/Kg

4. REFERENCES

 Table 4 Comparison of Primary Batteries [8]

Lithium-carbon	Polycarbon	т:	$xLi + CFx \rightarrow xLiF + xC$ (overall reaction)	281/	200-600 W-h/Kg
monofluoride	fluoride	LI	$xL_1 + CFx \rightarrow xL_1F + xC$ (overall reaction)	2.0 V	200-600 W-h/Kg



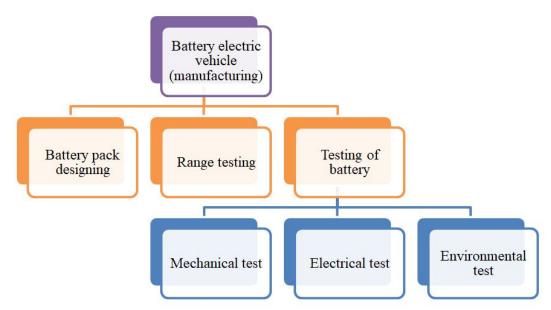


Fig. 19 Summarizing BEV Manufacturing [7]

Secondary batteries	Cathode material	Anode material	Electrolyte/reaction	Nominal voltage (V)	Practical capacity (W-h/Kg)
Lead-acid	PbO ₂	РЬ	H_2SO_4 aqueous solution $Pb+SO_4^{2-} \leftrightarrow PbSO_4+2e^-$ (anode) $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \leftrightarrow PbSO_4+2H_2O$ (cathode) $PbO_2 + PbSO_4+Pb \leftrightarrow PbSO_4+2H_2O$ (total reaction)	2	30-50
Nickel- cadmium	NiOOH	Cd	KOH aqueous solution $Cd + 2OH^{-} \leftrightarrow Cd(OH)_2 + 2e^{-}$ (anode) $2NiOOH + 2H_2O + 2e^{-} \leftrightarrow 2Ni(OH)_2 + 2OH^{-}$ (cathode) $2NiOOH + Cd + 2H_2O \leftrightarrow Ni(OH)_2 + Cd(OH)_2$ (total reaction)	1.2	50
Nickel- metal hydride	NOOH	Hydrogen absorbed alloy	KOH aqueous solution $H_2+2OH^{-}\leftrightarrow 2H_2O +2e^{-}$ (anode) $2NiOOH +2H_2O +2e^{-}\leftrightarrow 2Ni(OH)_2 +2OH^{-}$ (cathode) $2NiOOH +H_2\leftrightarrow 2Ni(OH)_2$ (total reaction)	1.2	100
Lithium- ion	LiCoO2	C+Li/Li	$\begin{array}{l} Organic electrolyte with lithium salt\\ Li(C) \leftrightarrow Li_{(1-x)}(C) + xLi^+ + xe^{\cdot} (anode)\\ xLi^+ + xe^+ Li_{(1-x)}CoO_2 \leftrightarrow LiCoO_2 (cathode)\\ Li(C) + Li_{(1-x)}CoO_2 \leftrightarrow LiCoO_2 (total reaction) \end{array}$	1.6	150-200
Lithium- sulfur	S	Li	$\begin{array}{l} \text{Liquid electrolyte} \\ \text{Li}_2\text{S}_8 + 2e^- + 2\text{Li}^+ \leftrightarrow 2\text{Li}_2\text{S}_4 \\ \text{Li}_2\text{S}_4 + 2e^- + 2\text{Li}^+ \leftrightarrow 2\text{Li}_2\text{S}_2 \\ \text{Li}_2\text{S}_2 + 2e^- + 2\text{Li}^+ \leftrightarrow 2\text{Li}_2\text{S} \end{array}$	2.15	2600-2800
Lithium- air	LiCoO ₂	С	Liquid or gel electrolyte 2Li +O ₂ ↔Li ₂ O ₂ 4Li + 6H ₂ O +O ₂ ↔4(LiOH.H ₂ O)	3.1	3620-5200

Table 5	Comparison of Secondary Batteries	[8]