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Electrolyte in Sodium-ion Battery-Modelling and Simulation

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Abstract

The design and manufacturing of energy storage system (ESS) are essential for human society development. India has made significant efforts to improve its energy storage infrastructure. The main elements for energy storage development are batteries i.e., lithium-ion batteries (LIB), lithium air batteries, etc. and supercapacitors. As the lithium resources are specifically located in China, Japan, USA, and Chile, to reduce the dependency on these countries for lithium-ion battery, India must think about alternative material. Sodium-ion battery (SIB) is at the forefront of the development, and it aims at providing low-cost devices less affected to resources. This review paper addresses the fundamental principles, structure and focused on the components of sodium-ion battery. This paper also helps to address the electrolytes used in sodium-ion battery with their design and modelling. Current research and future directions has been discussed in this article for sodium-ion batteries.

Keywords: *Energy; batteries; sodium; supercapacitors; development; electrochemical*

1.0 Introduction

Lithium-ion batteries (LIBs or Li^+) has become an essential component of the present time of energy storage system (ESS). As the global leader has raised their concern regarding environmental pollution using LIBs has been increasing significantly. In the last five years, growing demand of electric vehicles, portable devices also lead to increased dependence on these batteries[1]. Now-a-days renewable energy systems (RES) i.e., solar photovoltaic, wind or water, power systems have grown in popularity across the world. Grid stability difficulties are one of the issues that arise when RES penetration grows[2]. The growth of electrical energy storage (EES) devices is very essential for the efficient use of renewable energy storage. EES devices can play significant role in grid stability in several ways[2-4]. Developed nations like Japan, United States, Germany, and Australia have developed extensive electrical energy storage systems, while developing nation China's work is in progress[5-7]. In the battery energy storage system, the storage isolator offers electrical separation between the storage system and the grid. Power converters are the devices which allows the bidirectional flow of power and control of it depending on load scheduling. In case of extra power generation, power converter can charge storage system from AC to DC while in case of peak hours, the reverse process can also be done[8-9]. The term battery management system (BMS) is used to monitor and control the various operating parameter of batteries like overcharging, over-discharging. The function of BMS is to provide safe operating range by minimizing over-charging and over-discharging. Table 1 compares several grid size battery systems[4].

The lithium-ion battery demand and cost are increasing, which decreases the availability of lithium-ion battery on earth. So, we must introduce the new form of battery i.e., sodium-ion battery.

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Table 1: Different types of battery system

Types of Battery	Energy density (m”^{1}kgs”^{2})	Self-discharge % per day	Cycling	Cycle efficiency %	Cost $/kWh
Lead-acid	50-90	0.1-0.2	500-1800	70-90	200-400
Lithium ion	200-500	0.1-0.3	1000-20000	75-97	600-3800
Sodium-sulphur	150-300	0	2500-4500	75-85	300-500
Nickel-Cadmium	60-150	0.2-0.6	2000-3500	60-83	800-2400

Sodium-ion batteries (SIBs or Na^+)

In 2010’s and 2020’s, sodium-ion batteries received much attention because of its properties which offers high abundance nature, ease of transport and its low cost. This property makes it so efficient among all rechargeable batteries like Li-ion battery. Table 2 shows the comparison between LIB and SIB[10]. Sodium (Na) is the fourth most available material on the earth crust and cost of sodium make it suitable material for the energy storage devices. Other parameters like ambient temperature operations, nontoxic and ease of disposable make it suitable for energy storage devices. There are massive quantities of sodium precursors which includes twenty-three billion tonnes of sodium carbonate (soda ash) is present in the country in North America[11]. According to the technical report of India Stationary Energy Storage Market (IESA) from 2008-2026 (Fig.1), noticed that the cost of the sodium-ion batteries is decreasing continuously as the technology is upgrading. Cathode, anode and electrolyte are the components of sodium-ion battery, where simulation is very important part to enhance the sodium-ion battery electrolyte.

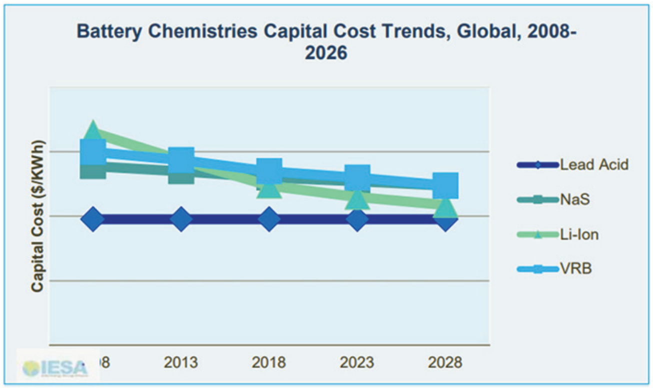

Figure 1: Battery chemistries capital cost (2008-2026) (Source: IESA)

Table 2: Comparison between LIB and SIB

Parameters	Lithium-ion battery	Sodium ion battery
Cation radius	0.76	1.06
Atomic weight	6.9gmol^{-1}	23gmol/1
Melting point	180.5	97.7
Coordination	octahedral and tetrahedral	octahedral and prismatic
Theoretical capacity of metal electrodes/mAhg^{-1}	3861	1166
E° (vs. Li/Li^+)	0	0.3
Theoretical capacity of metal electrodes/mAhcm^{-3}	2062	1131

2.0 Energy Storage Market in India

India has expanded its manufacturing market of electronic gadgets to meet the local demands. Lithium-ion batteries and supercapacitor are in high demand in India, because of the country’s rapid development in electronics, particularly in portable electronic items. Electronic gadgets, camcorders, self-start vehicles, electric vehicles (EV), solar energy harvesting/storage modules, power supply, and other innovative applications have increasing demand since they require quick charging and discharging facility. Super capacitors are popular in the automotive and energy storage industries, particularly for usage in EV and hybrid electric vehicles (HEVs)[12]. Table 3 shows the manufacturing production market of supercapacitor and lithium-ion battery in India.

Reliance industry is the big manufacturer of the sodium-ion batteries in India, as the Indian conglomerate Reliance Industries has paid $135 million to purchase Faradion, a UK start-up developing sodium-ion batteries. Since 2015, India has significantly expanded its mobile producing units, with roughly 118 units of mobile handset producing plants.[12] According to emerging technology news (ETN) projections (Total Energy Storage Market Overview) indicate a capacity of 196 GWh and 250 GWh for grid scale, behind the meter and railways by 2019-2027 as shown in Fig.2. It shows that there is an increment of grid scale and BTM at 250 GWh. Mobile device manufacturing increased from 60 million units worth $2.9 billion in 2014–2015 to 225 million units worth $20.3

billion in 2017–2018. The manufacturing unit of LCD and LED TVs is climbed from 8.7 million in the year 2014–15 to 16 million in the year 2017–18. LED goods manufactured in India increased in value from $334 million in 2014–15 to $1.5 billion in 2017–2018[12]. Recent IESA projections indicate the growth of annual installation energy storage capacity by 2026 (Fig.3).

Table 3: Manufacturing industries of supercapacitor and lithium-ion battery in India

	Sodium ion	Lithium ion
1.	Tirupati Internationals, Delhi	Samsung SDI Co. Ltd.
2.	Electronicon System Electric, Nashik	Panasonic India Pvt. Ltd
3.	Saison Components and Solution, Delhi	Sony India Pvt. Ltd.
4.	SPEL Technologies, Pune	Amco Saft India Ltd.
5.	MG Automation Technology, Nagpur	LG Polymers India Pvt. Ltd.
6.	Santronic, Mumbai	Coslight India Telecom Pvt. Ltd
7.	Simwayon Power, Noida	Semyung India Enterprises (Pvt.) Ltd.
8.	Nikhil Electrolytics, Bhiwani	Rajamane Telectric Pvt. Ltd.
9.	–	ACME Cleantech Solutions Pvt. Ltd.
10.	–	Exide – EV

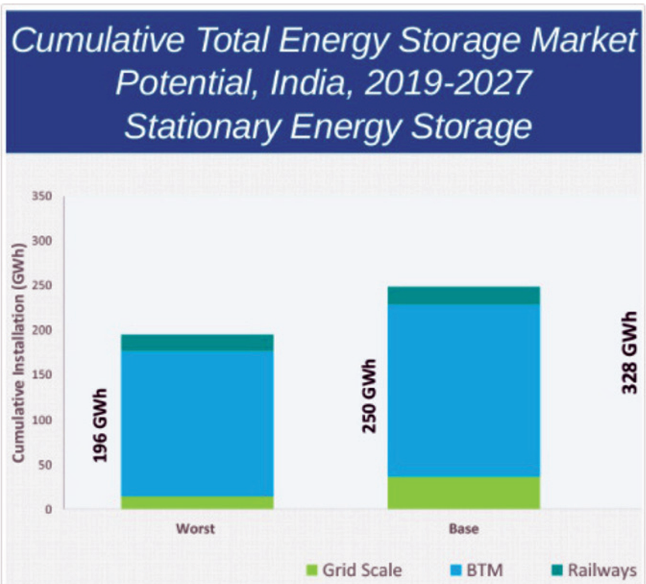

Figure 2: Total energy storage market potential, India, 2019-2027 (Source: ETN)

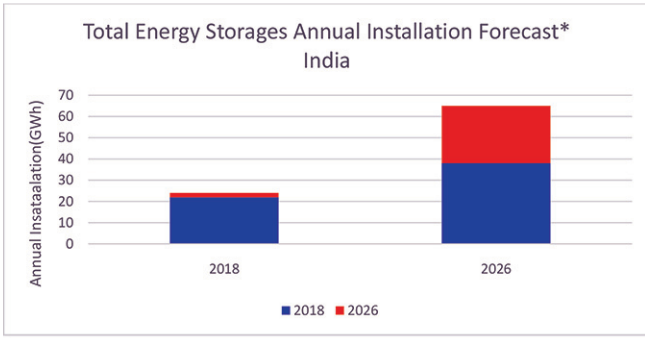

Figure 3: Total energy storage annually installation forecast (Source: IESA)

Supercapacitors are in great demand and are expected to reach about $8.33 billion by 2025 with a 30% compound annual growth rate (CAGR), with demand from the vehicle and energy industries accounting for 11% and 30 %. The market of LIB in India, is expected to reach 6000 crore rupees by 2022, owing to rising adoption of mobile phones, camcorders, cameras, and other electronic devices, electric vehicles, as well as an increment in the units of solar energy and wind energy projects in the country. Furthermore, as e-rickshaws become more widely used as public transportation in India, demand for lithium ion batteries is likely to increase rapidly over the next five years[12]. Fig.4 shows the pumped hydro storage system accounts for 92.6% at 171.03 GW of all currently installed forms of energy storage technologies (ESTs). Among all the EES technologies, LIBs made up the largest installed capacity of about 89% (8.5 GW)[13].

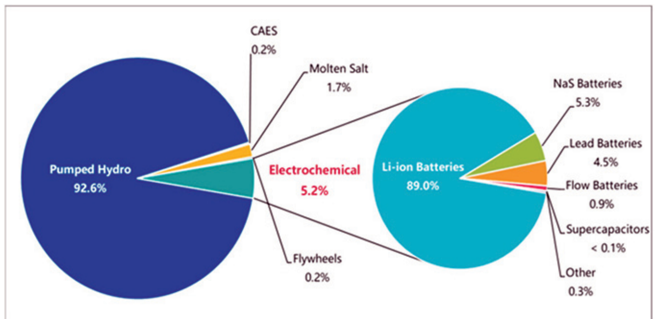

Figure 4: Representation of Global total operational ESTs project capacity (MW). Source: CNESA Global Energy Storage Project Database[13]

3.0 Opportunities and Challenges in Current Storage Technology in Indian Context

In the context of India, the opportunities are in electric vehicle, grid storage system and electronics while challenges are cost effectiveness and recycling.

3.1 Electronics Devices

The energy range for mobile electronics is 10–100 Wh. In the electronic appliances, the battery must be smaller and lighter, long cycle life, higher energy, and power density. In electronic appliances, the cathode materials used in lithium-ion batteries are lithiated transition metal spinel oxides, lithiated layered transition metal dioxides, and lithium metal phosphates.[14] To fulfill the voltage and current level for a specific application, two and more lithium-ion cell can be connected in series and parallel, and that battery module is incorporated into the device. And also, lithium-ion batteries used in mobile devices face three major challenges: (1) material having high energy and power density for electrode, (2) low cycle life at high charging rate, and (3) sensitivity of performance and storage on temperatures[14]. According to grand view research (Fig.5), the electronic market will be increase from 2014-2025. It has been shown in the graph, the growth of mobile phones is increasing day by day with the increasing demand of human beings[15].

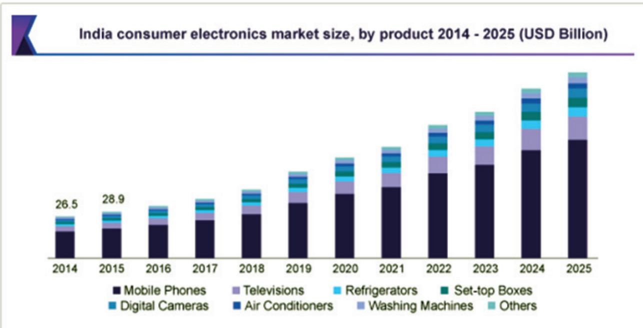

Figure 5: Electronic market in India[15]

3.2. Electric vehicles

India is the second largest populated country in the world which accommodate about 1.3 billion humans. As the India GDP is growing at 7% annually which is higher than developed countries. It means the demand of vehicles for transportation will also increase. The cells of major automobile companies like Maruti, Hyundai, Toyota choose that the petrol and diesel vehicle of these company the demand of vehicle will increase day by day and also leads to the environmental pollution. As the world leaders take oath to use the green technology for their development. In that context, India provides the subsidies for electric vehicles that will also lead to make popular electric vehicles. Recently, Tata has announced that it has sold out 1 lakh unit for four wheelers in consumer segment in year 2021. HEVs and plug-in hybrid electric vehicles (PHEV) allows decrease their reliance on liquid fuels while also lowering carbon di oxide emissions. The cost (cells, management, packing materials etc.) and performance (energy density, power density, cycle life etc.) are the two challenges in the electric vehicles. General Motors (Volt PHEV), Toyota (Prius HEV), and Nissan (Leaf EV) have all had commercial success using manganese spinel Li-ion technology in recent years[16].

3.3 Cost

To determine the commercial values of electric vehicles, cost is the important factor which vary with the production volume. The cost of nickel-cobalt-aluminium (NCA) is a cathode material is 15kWh depends upon original equipment manufacturer (OEM) ranges from $ 650 to $ 790/kWh which is very high than $250/kWh given by United States Advanced Battery Consortium (USABC)[17]. In recent it has been shown by department of engineering (DOE) that the cost of battery has been fallen from the year 2007 to 2012 i.e., USD 1,300/kWh to USD 500/kWh, although they are still far from the DOE's objectives of USD 300/kWh in 2015 and USD 125/kWh by 2022[18]. Sodium-ion (Na^+) and magnesium ion (Mg^{2+}) are attractive possibilities for low-cost battery. Because sodium consists bigger ionic radius and has a lower operating voltage (low energy)[14].

4. Sodium-ion batteries and their development

Sodium (Na) is known to be the fourth most abundant element on the earth.[10] Supply chain of sodium is very huge contains around twenty-three billion tonnes of sodium carbonate (Na_2CO_3) in the United States (US). In general, sodium-ion battery (SIB) is becoming a research topic in recent years,and it is becoming an alternative for lithium-ion battery (LIB). Because in 2010, it has been reported that the production of sodium carbonate is about USD 135-165 per tonne while lithium carbonate (Li_2CO_3) contains USD 5000 per ton[19-20]. Sodium-ion batterieswere researched when LIBs were first developed in the year 1970 and 1980, but they were mainly abandoned due to quick breakthroughs in the creation and progress of the commercial uses of lithium-ion batteries[21-27]. The reason was the materials, electrolytes and the glove box were insufficient to handle the sodium during those years and it makes the electrode performance difficult to evaluate. In the year of 1980, United states and Japanese designed the businesses of sodium-ion batteries (SIBs) in full cell before to the introduction of LIBs by using a lead-sodium alloy composite as the anode and for cathode materials P2-Na_xCoO_2 is used[28]. Hence, SIB are not designed with the sodium metal which causes formation of dendrites and passivation layer on anode material. Sodium offers a low melting point about 97.7°C causes safety problems for devices using sodium metal electrodes at ambient condition temperature. The components (cathode, anode, and electrolyte) of sodium-ion battery are illustrated in Fig.6.

The leaders of SIB are Faradion Limited, AGM Batteries Ltd, NGK Insulators Ltd, TIAMAT SAS, HiNa Battery Technology Co. Ltd, Altris AB, and Natron Energy Inc. etc. In recent, January 2022, a wholly owned subsidiary of Reliance Industries announced that its Reliance New Energy Solar (RNES) has entered into an agreement with British company Faradion and Reliance acquires 100% shareholding with total value of GBP 94.42 million. The company also revealed that Reliance will use Faradion's technology at its proposed giga-factory as part of the Dhirubhai Ambani Green Energy Giga Complex project at Jamnagar in western India[29]. Fig.7 describe the market of sodium-ion battery globally[30].

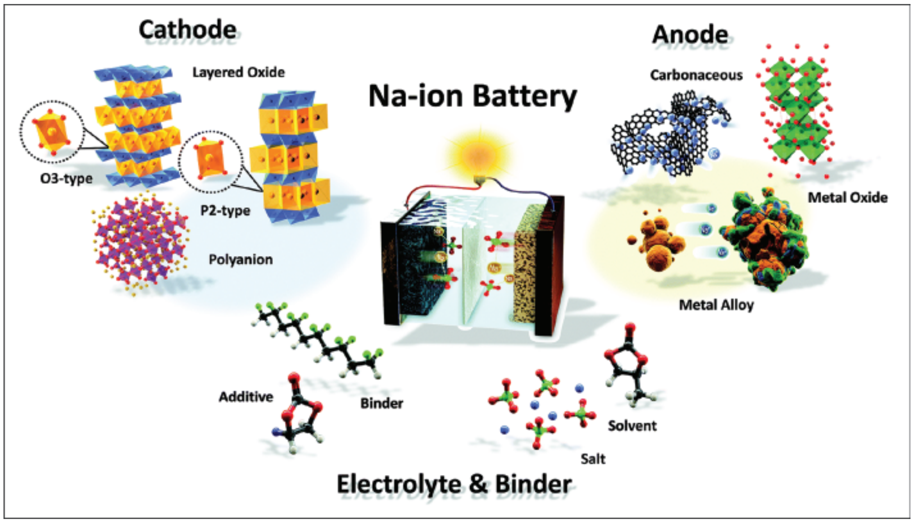

Figure 6: Brief description of sodium ion battery[28]

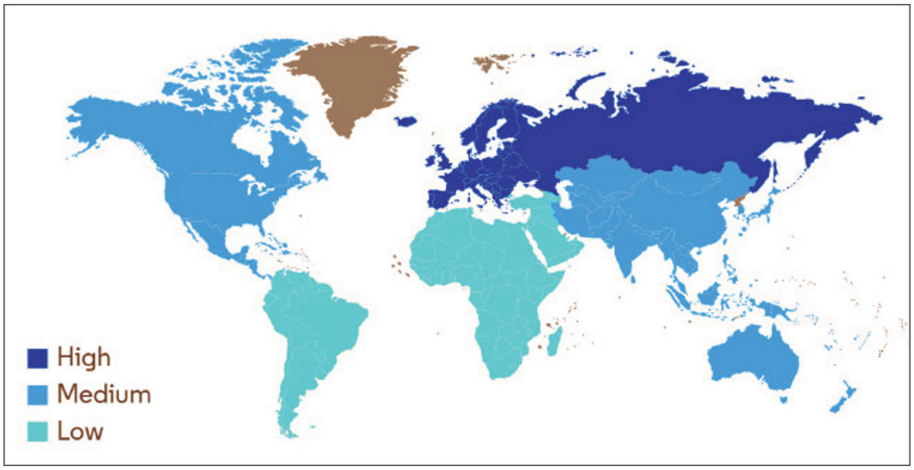

Figure 7: Global Market of Sodium ion battery and its development[30]

4.1 Components of Sodium-ion Batteries

4.1.1 Anode Materials

For the successful fabrication of the sodium-ion battery, it's difficult to identify the negative electrode. In comparison with lithium metal anode, metallic sodium has the lower theoretical specific capacity i.e., 1166mAhg^{-1} and higher standard reduction potential. In lithium metal anodes, the problem arises when the reactivity of sodium metal reacts with organic electrolyte solvents which causes the creation of dendrites during deposition of sodium metal. At low melting point of sodium 98ºC shows the safety problems in devices at ambient temperature by using a sodium metal electrode. Hence, making sodium full cells at this early stage in this area is quite challenging. Carbon based such as graphite, Metal Oxide Anode Materials, Intermetallic Anode Materials i.e.,SnSb/C nanocomposites considered as the sodium-ion anode materials[10]. Wang and team[31] reported that during the discharge process, the thin layer of nickel antimony (NiSb) deposited on the surface of sodium metal. This thin layer of NiSb was discovered to govern the uniform electrochemical plating of Na metal offering dendrite free and low overpotential plating of Na metal for more than hundred hours with the areal capacity of 10 mAhcm^{-2}. Graphene janusparticles were utilized to enhance the energy density. Interaction sites are provided on one side, while interlayer isolation is provided on the other and the energy density was 337 mAh/g[32].

4.1.2 Cathode materials

From the last few years, several tries have been done to develop the sodium-ion cathodes. In comparison with lithium-ion cathodes, sodium-ion also stores sodium by an intercalation reaction process. Sodium transition metal oxides are the promising cathode materials having high tap density, high working potentials, and capacity. To maintain its cost, several research progresses have been made to avoid using the expensive components such as cobalt (Co), chromium (Cr), nickel (Ni), or vanadium (V) in oxides. In 2012, P2-type

$Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ oxide made from earth-abundant iron (Fe) and manganese (Mn) resources was shown to reversibly store 190 mAh/g at 2.75V versus Na/Na^+ by using the $Fe^{3+/4+}$ redox pair[33]. $Na_{0.67}Mn_{1-x}Mg_xO_2$ has been used as a cathode material for SIBs with a discharge capacity of 175 mAh/g. Polyanion cathodes is also becoming an option for the developing cathodes in sodium-ion batteries, because the stronger covalent bond of polyanion offers to improve cyclicity and safety. Sodium vanadium phosphate[34] and fluorophosphates[35] are two polyanion-based cathodes that have shown outstanding cycle stability, with the high capacity of 120 mAh/g at 3.6 V against Na/Na^+.[36].

4.1.3 Electrolytes

It will also be important to develop adequate liquid electrolytes in combination with anode advancements, which is an excellent research opportunity. Aqueous electrolyte and non-aqueous electrolyte used in sodium-ion batteries. When aqueous electrolyte used in sodium-ion batteries, the electrochemical stability window shows the lower voltage and limited energy. To increase the voltage, non-aqueous electrolyte can be used. Sodium hexafluorophosphatee ($NaPF_6$) or sodium perchlorate ($NaClO_4$) can be used as salts in organic carbonate polar aprotic solvents used in Li^+ electrolytes notably propylene carbonate (PC) for sodium batteries. Komaba[28] and team described that based on XPS and TOFSIMS data, the formation of solid electrolyte interface (SEI) on hard carbon is an inorganic salt and contains precipitated species. Thomas et al.[37] used $NaClO_4$ in ethylene carbonate (EC) and shows that the SEI formed on carbon i.e. sodium carbonate (Na_2CO_3) and sodium alkyl carbonates (NaAC). And electrolyte additives improve the performance of the battery.

4.1.3.1 Role of Electrolyte in Sodium-ion Battery: Modelling and Simulation

This section highlights the efforts made from simulation and modelling aspect to develop the performance of sodium-ion battery electrolytes. Liquid electrolyte, polymer electrolyte, ceramic, glass, and solid-state ionic materials simulation will be discussed in this section[38].

Liquid electrolytes are the common electrolytes used for SIBs. The basic component of liquidelectrolyte is like the lithium-ion battery,and it involves the salts like Li-ion salts. As a result, there are no methodological differences from a computational perspective, and much research has been done for LIBs can reuse[38]. According to Liu et al.,[39] they observed the variations in energy, enthalpies, and free energies during the reduction process of common electrolytes such as ethylene carbonate (EC), propylene carbonate (PC), and vinylene carbonate (VC) by using density functional theory (DFT). The reduction process of VC forming $(CHCHCO_3Na)_2$, EC shows decomposition to $(CH_2CH_2CO_3Na)_2$, and PC shows reduction to $(CH_2CH_2CH_2CO_3Na)_2$ having Gibbs free energy (ΔG) is –974.8 kJ mol^{-1}, –874.7 kJ mol^{-1}, –970.4kJ $mol^{-1}$and concluded that the order VC<PC<EC is the same as experimentally observed for LIB electrolytes for one-electron decomposition[39-40]. While, in case of two-electron decomposed into Na_2CO_3 showing ΔG = –1424.5, –1420.9, and –1345.9 kJ mol^{-1}, order gets reversed; EC>PC>VC. It should be noted that one-electron decomposition is changed for lithium-ion battery; VC>EC>PC, but there is no change in two-electron decomposition. Hence, the change in ΔG decreased in lithium-ion battery[41]. There are various reduction research studies on EC, PC, and VC has been done till now in addition of fluoroethylene carbonate (FEC) using DFT[39].

Apart from the liquid solvents, the role of sodium-ion salts shows great importance for sodium-ion battery electrolytes. the strength of SIB electrolyte is the interaction of cation and anion. Because of the interaction of cation-anion, it shows the direct impact on ionic conductivity[42]. About 53 anions are present in cation-anion interaction involves fluoride ion (F^-), chloride ion (Cl^-), nitrate (NO_3^-), weakly interacting anions like hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), perchlorate (ClO_4^-), etc. were studied by DFT theory and this method is studied by Jonsson and Johansson[43]. Na-2,5,8,11-tetraoxatridecan-13-oate (TOTO) is a saltused as a solvent, and the TOTO anion becomes 2,5,8,11-tetraoxatridecan-13-oate[44]. Recently developed sodium salts is basically based on nitrile chemistry having weak coordinating anions, showing ion-ion interaction energies and the calculation is done by DFT[45]. Salts such as sodium pentacyanopropenide (NaPCPI), sodium 2,3,4,5-tetra-cyanopirolate (NaTCP), and sodium 2,4,5-tricyanoimidazolate (NaTIM) were calculated computationally and experimentally versus sodium bis (trifluoromethylsulfonyl) imide (NaTFSI) and $NaPF_6$. The results shows that the ion-ion interaction of NaPCPI, NaTCP and NaTIM shows weaker ion-ion interaction than NaTFSI and $NaPF_6$. And according to the experimental data, the highest ionic conductivity was observed for the electrolyte based on NaTCP, having the weakest ion–ion interaction[38]. Researcher Okoshi and team investigated the two large DFT study on sodium-ion solvation in 27 sodium-ion battery solvents[46-47]. Shakourian-Fard et al[48]. studied the largest sodium-ion solvent interaction by considering complete first solvation shells where the geometries were taken from molecular dynamic study and calculation was done using DFT. A comprehensive research study of lithium ion and sodium-ion against crown ether done by De et al[49].

Polymer electrolytes have mobile ions dissolved in a polymeric or macromolecular solvent. It involves liquid components in gels, plasticized systems, and inorganic nanoparticles[50-52]. Poly (ethylene oxide) (PEO), shows the great research interest since 1970s[53-54], in both lithium-ion electrolyte[55-56] and sodium-ion conducting electrolyte[57].

Other polymers such as polycarbonates[58], and polyacrylonitrile[59] used as solutions for sodium-ion conducting materials. Polymer electrolyte cation dynamics can be stimulated by Monte-Carlo (MC). The Monte-Carlo simulation can predict the Vogel–Tammann–Fulcher (VTF) conductivity behaviour of polymer electrolytes[60-61]. Different oligomer model of PEO, can be applied on DFT of short-chain poly (ethylene glycol) (PEG) with various alkali metal cations, including sodium-ion[62]. Hence, these oligomers have 18 repeating units equivalent to PEO with hydroxyl end-groups. Many simulations have been done to show the interaction between cation and polymer host which reduces the influence of anion[62].

The modelling and simulation of ceramic and glass sodium-ion conducting material follows the great research interest in sodium electrolyte. β-alumina structures have been focused since 1980s and 1990s[63-68], on silicate glasses[69-71] and sodium (Na) super ionic conductor (NASICON)[72-74]. Interest on borohydrides[75-76] and phosphosulfides[77-78] also shows the great research interest. Classic molecular dynamics (MD), density functional theory (DFT), ab initio MD (AIMD) are the main techniques shows the research interest in various domains. Beta-alumina (β-alumina) and β"-alumina electrolytes belongs to the class of stoichiometric or nonstoichiometric aluminum oxide include sodium-ion (Na^+). According to researcher Zendejas[65] and Thomas[64], investigated the sodium-ion conduction in both β- and β" -alumina. Researcher Smith and Gillan[79] also performed MD simulations of Na^+- β"-alumina.Beckers and team[63] used FF together, classical and molecular dynamics techniques also used to stimulate the structures of β-alumina, likediaoyudaoite ($Na_2Al_{22}O_{34}$) and others.

5.0 Conclusion

With an average GDP growth rate of 7% over the previous five years, India is considered as one of the world's fastest rising economies and world's fastest-growing electronics market places. As the air pollution is increasing day by day our Indian leader are promoting electric vehicle for transportation, battery-based grid storage to fulfil the peak overload demand, battery-based application in stated of petrochemical fuel. Currently Li-ion battery is used in all electronic and electrical vehicle which are important from other countries like China, South Korea etc. As current geo-political relationship with China, India must think about alternative economical solution of Li-ion battery which also reduces dependency on a particular country. Sodium-ion batteries are very promising material in this context.

Electronics consumption is expected to expand at an exponential rate to $400 billion by 2023–2024. With the emergence of new items and an aspirational young generation, the demand for portable electronic gadgets is also increasing[12]. In the future decade, the demand for sodium-ion batteries will grow at an exponential rate. Sodium-ion batteries have high performance electrode materials, fast diffusion of Na^+ ions which shows the rate performance of sodium cells, safety at cathode current collector. But there some challenges associate with sodium-ion battery technology like low theoretical capacity of electrode, low cyclicity, low redox potential with respect to li-ion technology. But sodium-ion battery is much safer compared to LIB. Overall, the development of sodium-ion battery in India is also in progress and it is very important that it is in need to enhance the energy density which can be used for high power applications.

6.0 Conflict of Interest

The authors declare no conflict of interest.

7.0 Acknowledgements

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