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New Age Batteries: Recent Breakthroughs in Sodium-Ion Battery Technology

Kavy N Panchal
Delhi Private School Dubai
Guided by - Roopa Shankar

Abstract:- In this race to a decarbonized energy landscape, sodium-ion batteries have been pursued as a sustainable alternative to lithium-ion batteries. The abundance of the element, reduced production costs, and smaller impact on the environment compared to Li make SIBs a possible solution for large-scale energy storage. This work focuses on the current main components of SIBs, which include cathodes like layered transition metal oxides and Prussian blue analogues, and some state-of-the-art materials such as lithium-doped tunnel-type cathodes. Anodes include disodium terephthalate/multi-walled carbon nanotube composites and flash-pyrolyzed coal char that are discussed for the enhancement of their sodium storage capabilities. The performance assessment due to these different electrolytes is presented, among which are ethyl acetate-based ones and some solid-state NASICONs. Although challenges such as the low energy density and dendrite formation exist, ongoing research focuses on enhancing the lifespan, safety, and cost-effectiveness of SIBs so that broad adoption in a sustainable energy storage solution is achieved.

Keywords:- *Sodium-Ion Batteries (Sibs), Decarbonized Energy, Sustainable Energy Storage, Layered Transition Metal Oxides, Prussian Blue Analogues, Lithium-Doped Cathodes, Disodium Terephthalate/Multi-Walled Carbon Nanotube Composites, Flash-Pyrolyzed Coal Char, Ethyl Acetate-Based Electrolytes, Solid-State NASICON Electrolytes, Energy Density, Dendrite Formation.*

I. INTRODUCTION

Interest in advanced technologies of energy storage pursuant to the transition into a decarbonized energy landscape through the minimization of carbon footprints has therefore been heightened. Lithium-ion batteries, though making high-flying progress, are constrained by lithium resource scarcity, cost volatility, and safety concerns. A number of alternative energy storage systems thus attract growing interest for the performance, sustainability, and economic viability expected of them.

This, in fact, positions sodium-ion batteries with very compelling value propositions because of the abundance and homogeneity of sodium geologically around the globe.

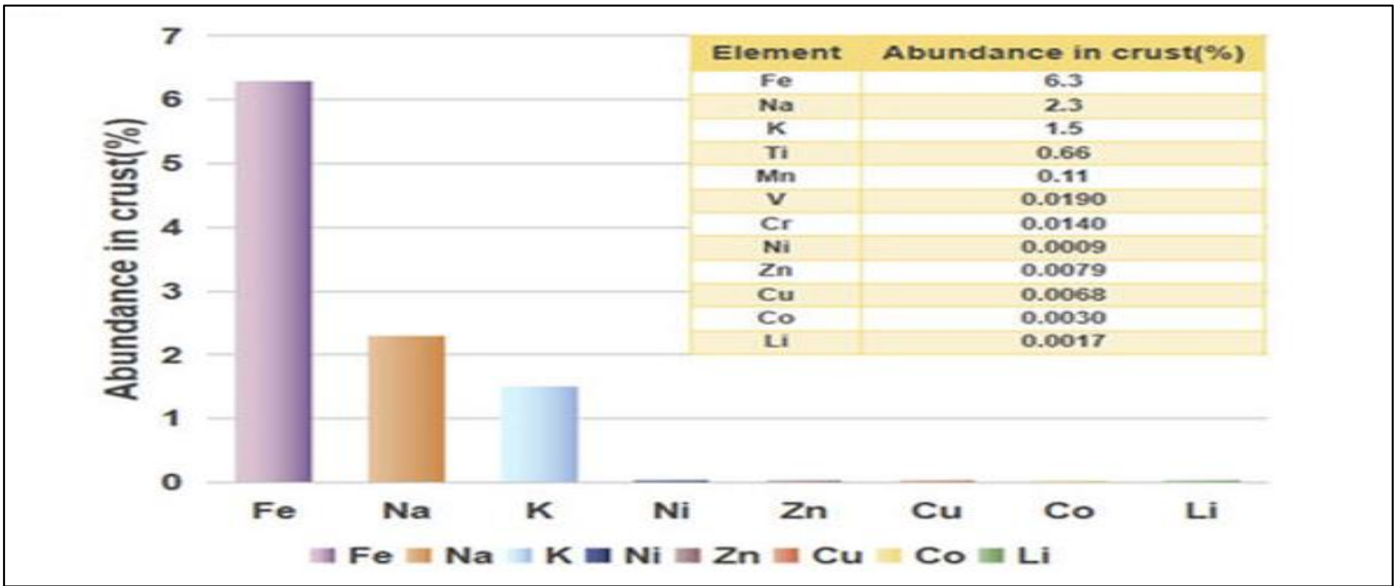

Fig 1: Statistics on Metal Reserves in the Earth's Crust

Sodium-ion technology, having lesser environmental impact and possibly lower production costs than their lithium-ion counterparts, may therefore be very promising for large-scale applications in energy storage. Electrochemical properties of sodium, though different from those of lithium, provide opportunities for the innovative development of electrode and electrolyte materials.

II. MATERIALS OF SODIUM-ION BATTERIES

SIBs take advantage of the high availability and low cost of sodium. Now let us discuss the potential electrodes and electrolyte for SIBs.

A. *Cathodes for SIBs*

Typical cathodes for sodium ion batteries include layered transition metal oxides with a general chemical formula of Na_xMO_2 with varying crystal structures as shown in Fig 1, polyanionic compounds, and Prussian blue analogues. These materials have to provide high energy density, excellent cycling stability, and capability for quick charge/discharge.

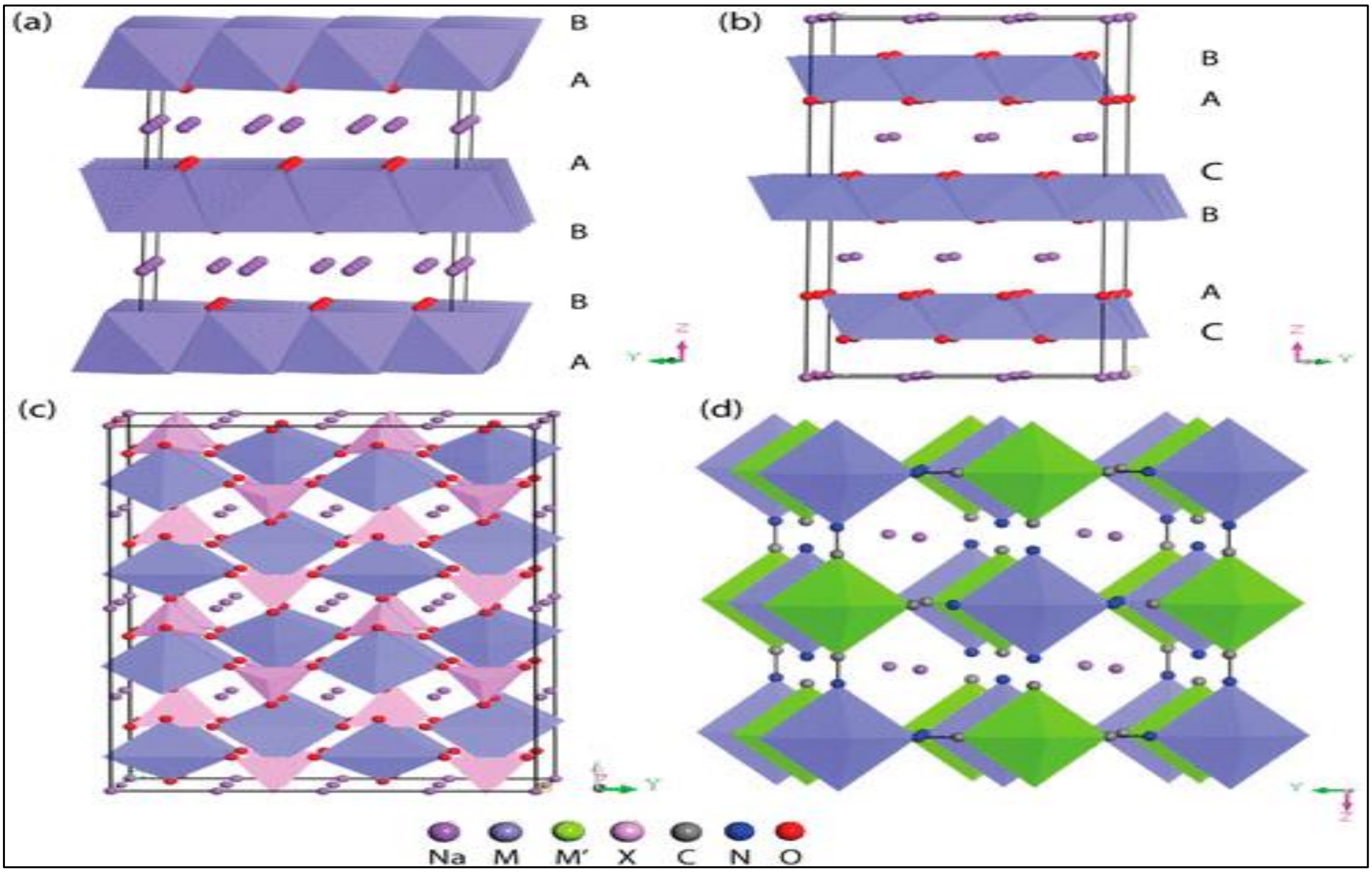

Fig 2: Crystal Structures of SIB Cathodes: (a) LTMO–P2-Na2/3MO2, (b) LTMO-O3-NaMO2, (c) Polyanion NaMXO4, and (d) PBA-NaMM′(CN)6.

➢ *Lithium Doped Tunnel Type Cathode*

Nanostructured tunnel-type $Na_{0.44}MnO_2$ (NMO) has garnered significant interest as a promising cathode material for Na-ion batteries due to its simple preparation process and low production cost. However, to address its limitations, a series of Li-substituted $Na_{0.44}Mn_{1-x}Li_xO_2$ samples were developed. Density functional theory (DFT) analysis revealed that Li substitution not only stabilizes the crystal structure but also enhances Na^+ ion diffusion during charge and discharge cycles. Additional calculations indicated that the introduction of Li improves the material's metallic properties, supporting efficient electron transfer.

The optimized $Na_{0.44}Mn_{0.94}Li_{0.06}O_2$ ($NMOL_{0.06}$) shows a relatively high reversible capacity of 106.1 mAh g^{-1} at 5 C, sustained over an impressive number of cycles. Most importantly, full cell using the $NMOL_{0.06}$ cathode and a commercial hard carbon anode has energy density as high as 257.2 Wh kg^{-1} and does not lose more than 83.6% of its capacity over 300 cycles at 1 C, convenient for real applications.

The major advantage of SIBs is however its independence from very limited Lithium reserves on earth and the usage for Lithium as doping might seem like it goes against the core idea of this paper. The lithium used in the SIBs developed with $NMOL_{0.06}$ electrode can be sourced from the previously made Li batteries and hence be sustainable in the sense of recycling as well as make a promising future battery.

➢ *Polyaniline Coated FeMnCu co-doped Prussian Blue Analogue*

Sodium hexacyanoferrate (Prussian Blue) has emerged as a electrode for sodium-ion batteries (SIBs) due to its high theoretical capacity and ease of synthesis. It does suffer from issues like structural instability and low electronic conductivity. To address these limitations, recent research has focused on the development of modified PB materials.

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Xin Xu et al. proposed a novel strategy involving FeMnCu tri-doping and a conductive polyaniline (PANI) coating. The FeMnCu doping enhances the structural stability and electronic conductivity of the PB framework, while the PANI coating further improves the rate capability. This synergistic approach resulted in a FeMnCu@PANI core-shell structure that exhibited superior electrochemical performance, including high specific capacity, excellent rate capability, and prolonged cycle life.

The non-toxic nature, high yield, and low cost of the FeMnCu@PANI composite make it a promising candidate for large-scale applications in SIBs. This work highlights the potential of rational design and multifunctional materials for advancing the development of high-performance energy storage devices.

B. Anode Materials

➢ *Disodium Terephthalate/Multi-Walled Carbon Nanotube Composite*

Due to their inherent advantages associated with simple preparation methods, recyclability, and multi-electron reactions, the focus is currently on organic materials as SIB anodes. Cheng Han et al. have prepared a disodium terephthalate/multi-walled carbon nanotube organic composite using an anti-solvent method for use as an SIB anode material. The experimental results indicated that the optimum sodium storage can be made at a dosage of 10 wt% MWCNT, where the reversible capacities reached 229.9 and 93.2 mA h/g at current densities of 0.1C and 2C, respectively. After 50 cycles, a capacity of 124.9 mA h/g was sustained at a current density of 1C.

➢ *Flash-Pyrolyzed Coal Char*

Coal char is an ultra-low-cost hard carbon with very promising applications as an anode material in SIBs. In flash pyrolysis, char is heated to 1000 °C/s in a drop-tube furnace, making the structure highly irregular. Compared with traditional slow-pyrolyzed char electrodes, the flash-pyrolyzed char has a larger d-spacing and a smaller closed micropore diameter, which increase the capacity of the anode. The replacement of the traditionally used ester-based electrolyte by an ether-based one increases the anode performance of flash-pyrolyzed char in sodium-ion batteries. This will improve not only the initial Coulombic efficiency from 58% in the ester-based to 64% in the ether-based electrolyte but also the specific capacity under such an ether-based electrolyte. This combination of flash pyrolysis and ether-based electrolyte increases the sodium-ion battery discharge capacity of coal char by more than 50%, from 72.5 mAh g −1 of the slow-pyrolyzed char in ester-based electrolyte to 109.4 mAh g −1 for the flash-pyrolyzed char in ether-based electrolyte at a 50 mA g −1 discharge rate.

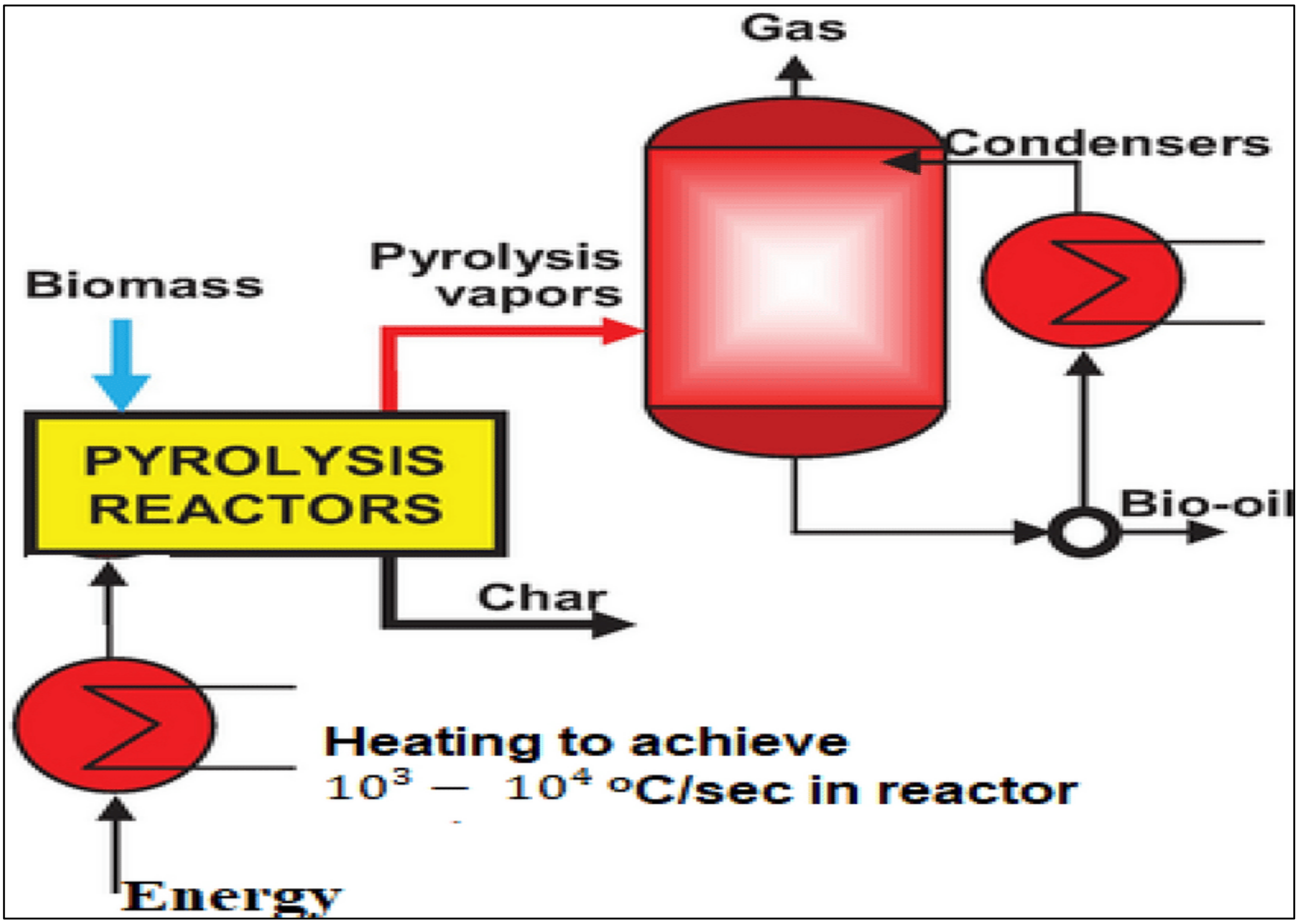

Fig 3: Flash Pyrolysis Reactor

C. Electrolyte

➢ *Ethyl Acetate Based Electrolyte*

A new non-aqueous ethyl acetate-based electrolyte was developed for sodium-ion batteries. This electrolyte, having a unique bulk structure with poor solvating features, enabled stable performances of Na0.97Ca0.03[Mn0.39Fe0.31Ni0.22Zn0.08]O2/hard carbon pouch cells up to 4.0 V at high temperatures. Operation was prolonged by reducing cell failure mechanisms related to impedance growth, sodium plating, and gas evolution, along with thermal instability.

➢ *Solid State NASICON Electrolyte*

- NASICON—sodium superionic conductor, $Na_3Zr_2Si_2PO_{12}$—has been emerging as one of the most promising electrolyte materials in use for a sodium-ion battery because it has high ionic conductivity and excellent stability.

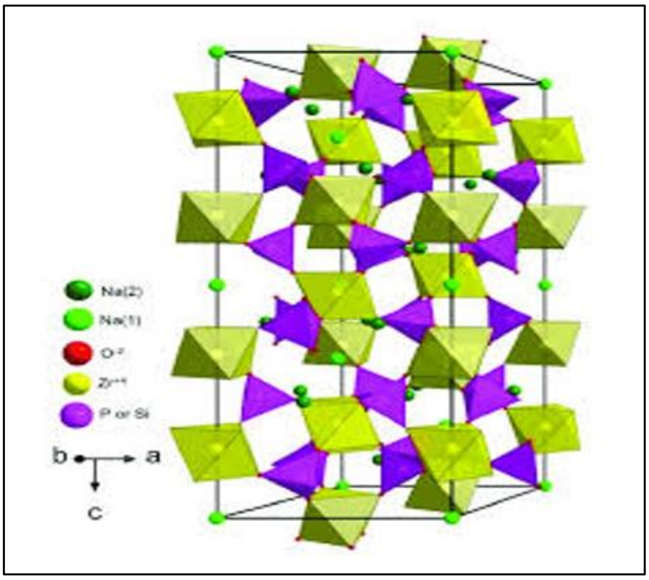

Fig 4: Rhombohedral Structure of NaSiCON

Doping strategies have been employed to enhance the ionic conductivity of NASICON-type solid electrolytes. The introduction of transition metal dopants has yielded sodium ion conductivities approaching 10^-3 S/cm. These improvements are attributed to the formation of lattice defects, conductive phases, and optimized crystal structures. Moreover, doping has been shown to enhance the electrochemical stability of NASICON, contributing to overall battery performance.

➢ *Gel Polymer Electrolyte*

A co-solvent of adiponitrile(ADN) with ethylene carbonate(EC) is proposed as an electrolyte solvent for the electrodes of a sodium-ion battery. S Praveen, S.A Hashmi et al. reported on the flexible thick film of a gel polymer electrolyte containing a Na-salt, namely, sodium triflate, dissolved in a mixture of ADN: EC entrapped in polyvinylidene fluoride-co-hexafluoropropylene, for applications in SIBs.

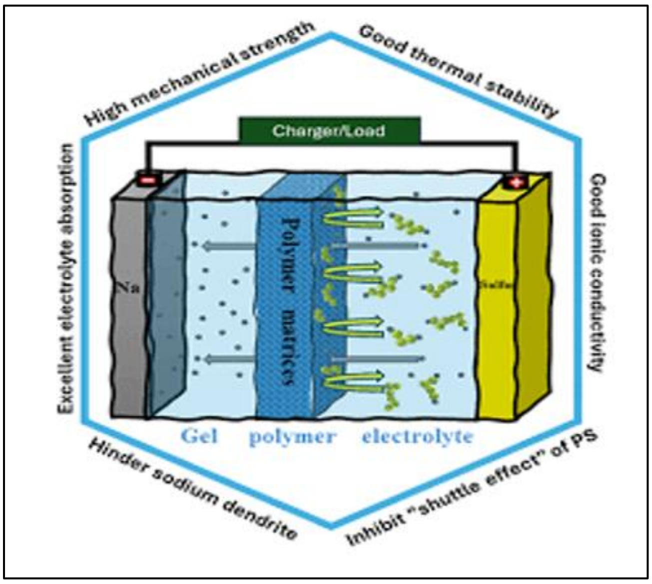

Fig 5: Graphic Showing Advantages and Basic Structure of GPE

They analyzed GPE film and did X-ray diffraction, SEM, and FT-IR spectroscopy. GPE film interposes metallic electrode planks then covers them with suitable electrolyte. Such Electrolyte show performance characteristics like the high ionic conductivity, the window of electrochemical potential is wide and has satisfactory thermal stability. However, combustibility of the used organic polymer is a major drawback. This could lead to serious issues as overcharging the battery could cause fires hence limiting the uses of the SIB until further improvements.

III. APPLICATIONS OF SODIUM ION BATTERIES

SIBs have been considered as an alternative to Li-ion batteries, based on the fact that sodium is an Earth-abundant element and thus inexpensive. Their availability will be beneficial in the sector such as the following.

A. Large Scale Energy Storage

After a proper structure for the SIB is developed, we can anticipate that they will be more affordable due to the reason mentioned above and hence SIBs will be more suitable for grid-scale energy storage.

B. Electric Vehicles

The EV market is dominated by LIBs since they don't have much competition; however, SIBs are aimed to be a more economical alternative. Enhanced energy density through improvement of cathode and anode materials will be imperative in this respect for SIBs.

C. Off Grid Power Systems

SIBs cost less, which is really useful in places that are either rural or not so wealthy. Often, these places also experience power cuts or blackouts. In these situations, we can use SIBs as power storages when we're off the grid.

IV. CHALLENGES AND FUTURE PROSPECTS

SIBs are considered as an affordable and sustainable energy source; however, they are still far from achieving commercialization.

A. Challenges

➢ *Energy Density*

Behind other batteries, SIBs do have less energy than the lithium-ion batteries. This fact mainly places an obstacle for large energy consumption device.

➢ *Electrode Material Development*

The search for a proper electrode material with a high capacity, large rate capability, and a long cycle life is quite challenging. In particular, for the design of the electrodes, the challenge is varied due to the huge size of the sodium ion compared to a lithium ion.

➢ *Dendrite Formation*

One of the most important concerns in the practical application of a sodium metal anode is the formation of sodium dendrites. Cyclic deposition/dissolution of sodium metal triggers the inhomogeneous solid electrolyte interphase layer, which encourages dendrite growth. In order to inhibit this issue, constructing an artificial protective layer on the sodium metal anode has become a very promising strategy.

A good protective layer shall have the following several properties. First, this should provide good passivation that will prevent undesirable reactions between the highly reactive sodium metal and the electrolyte. The layer must, secondly, be mechanically stable in order to support the mechanical stresses arising during cycling and avoid the formation of cracks in the SEI. Thirdly, it must have high ionic conductivity in order to facilitate the transport of sodium ions across the interface quickly. Finally, the protective layer should have low solubility in the electrolyte so that it would not dissolve during long-term cycling.

Several deposition technologies have been applied to coat protective layers homogeneously and attach to the substrate. Among them, some of these physical methods, such as spin-coating and doctor-blade coating, are comparatively easy yet likely to result in non-uniform coatings. Electrochemical techniques, involving in situ chemical plating and electrochemical corrosion, provide better control of layer formation but may be adversely affected by limited thickness and uniformity of composition. Cutting-edge techniques for deposition, such as chemical vapor deposition, magnetron sputtering, atomic layer deposition, and plasma-enhanced ALD, give ideal control of the layer thickness, composition, and microstructure, hence assuring better performance.

B. Future Perspective

- Improved number of life cycles: Further stabilization of the electrode materials and electrolytes is to increase the battery lifespan.
- Reduction of Costs: Optimized development in manufacturing, along with material costs, is to be optimized with SIBs to be commercially feasible.
- Safety Improvement: Resolution of the existing safety concerns, for example, dendritic growth and thermal runaway, is the key to enabling large-scale use of SIBs.

By this addressing these problems, humankind will benefit from the current progress of sodium-ion batteries becoming a leading technology in energy storage.

V. CONCLUSION

Due to the abundance of supply and relatively lower cost of sodium, SIBs have emerged recently as one of the most attractive alternatives for LIBs. Although huge efforts have been devoted to the improvement of electrode and electrolyte materials, their relatively lower energy density, limited cyclic life, and potential safety risks still constitute major concerns.

In this respect, further development is urgently needed for the complete fulfillment of SIBs: namely, the further search for a novel electrode material that could provide larger capacity with improved rate performance, the search for stable and efficient electrolytes, and further optimization of battery design and the manufacturing process. These innovations propose to solve a number of problems that are standing in the way of commercialization of SIBs for their wide uses in energy storage.

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