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Na-Air Battery: The Battery of the Future—A Review

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Abstract

Metal-ion batteries came into the limelight with the invention of Zn-ion battery as early as 1878, but its commercial viability came into picture in 1990 and lithium-ion cell in 1977. Since then, a number of metals have been experimented upon and similar rechargeable secondary storage batteries like Al-ion, Na-ion, Sn-ion, Mg-ion, K-ion have been developed. In this type of battery, electrochemical dynamics involves the movement of only one kind of ion between two electrodes (anode and cathode) during its charging and discharging. In spite of its advantages over earliest traditional batteries, it suffers from certain limitations like environmental incompatibility, cost economy, lower energy density, formation of solid electrolyte interphase, dendrite formation, thermal issues, decomposition of metallic electrodes, degradation of electrolytes, quick reduction in its efficiency, etc. To alleviate these issues, secondary energy storage units like metal-air batteries are now moving into limelight (the first MAB being Zn-air, which was commercialized in 1932), which reduces free air from atmosphere and oxidizes the metal anode (made of metals of alkali groups like Li, Na, Mg, Zn, etc.). They have better properties like higher energy density, higher theoretical specific capacity, light weight, better reversibility, longer life cycle, lower over-potential, higher round-trip efficiency, environmental friendliness, and cost economy etc. In spite of these benefits, it suffers due to its interdependency on various external and internal factors such as choice of electrolyte based on its compatibility with both electrodes for smooth ion transition for better conductivity, type of use, development of adequate potential at both electrodes, design of right electrodes, selection of right separator, selection of electrocatalysts and internal mechanism during charging and discharging etc. Hence, development of a full-proof metal–air cell still remains in its nascent stage. The current review work has been compiled in three parts, the first part reviews the general metal-air battery and its current status, the second part reviews research works done till now by various researchers on one of its components, that is, electrodes of metal-air battery) with reference to Na-air battery, and the third part deals with its other component, that is, electrolytes and current research. Then, the outcomes of various research works done so far on these three parts have been compiled in tabular form and critically analyzed. Finally, recommendations based on reviews of these latest research works have been outlined by the authors with few suggestions for future works.

Keywords: Metal-air battery, Na-air battery, air-cathode, electrocatalyst, energy conversion

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INTRODUCTION

Current global scenario in emission of greenhouse gases due to uncontrolled mining of metals necessary for the manufacturing of storage cells has raised a lot of concerns resulting in the continuous erosion of ozone layer in the atmosphere leading to the increase in earth's temperature. It has been roughly estimated that in order to meet the huge demand in battery sector, about 50% of total mined resources are being spent currently. Presently, the most popular form of secondary energy storage used in electric vehicle is Li-ion cell.

As per statistics (Statistic Research Department, October 24, 2023), China shares the highest 79% global production of Li-ion cell. In 2022, Australia was the leading producer of lithium by mining 61000 metric tons of lithium followed by Chile and China. Global reserve of lithium as per current reports is 60 million metric tons. With gradual spate in its annual consumption, it is forecast that present global reserve of lithium may last for less than three decades from now [1–8]. A typical electrical vehicle (EV) battery pack requires around 8 kg of lithium. Further report says that roughly 0.3 g of lithium is required to produce 1 ampere hour (1 Ah) of power. With the thrust of various governments globally and with a special mention of Government of India's aim towards complete transition of all its vehicular fleets into EV by the year 2030, India needs 120 GWh of Li-ion cells, which is itself a huge amount. To further aggravate environmental pollution, around 40000 tons of battery waste thrown uncycled every year, which could have been reused with adequate installation of recycling system, thereby reducing further mining.

Hence as a solution to this critical issue on one side and global eagerness for decarbonization and India's commitment to complete conversion of its fleets to EV system by 2030 in transport sector and similar commitments globally, there is an urgent need to find an alternative to current Li-ion system. Here, metal-air battery (MAB) comes to rescue with its intrinsic properties like low cost, light weight (indicating utilization of low quantity of metals and solvents), higher specific energy, higher power density, safety, higher capacity, sustainability and environmentally friendly to name some of its major attributes [9–15].

Functioning of Metal-Air Battery: A Brief Discussion

Basic function of a storage cell is to store and discharge energy by electrochemical reactions for its use during hour of need (Figure 1). Four main parts of a storage cell are (i) an anode (negative electrode) losing electrons by oxidation process; (ii) a cathode (positive electrode) gaining electrons and losing oxygen by reduction process; (iii) an electrolyte (aqueous/non-aqueous) medium, which helps in mobility of ions between two electrodes, when electrons ejected from anode surface moves via an external electric circuit to incident on the cathode surface during discharging; and (iv) a separator in form of a membrane, which separates anode from cathode and allows only ions to pass through it to reach the anode, obstructing mass transportation process between electrodes, thereby preventing short-circuit due to dendrites. Here, we are dealing with second-generation battery, called secondary battery, which functions under principles of reversible redox reactions. to name a few of these batteries, Li-air, Zinc-air, Na-air, Mg-air, Sn-air etc. [16].

Amongst the many qualities which differentiates a metal-ion from an MAB, most important one is the OER (oxygen evolution reaction) which occurs during the charging cycle and ORR (oxygen reduced reaction) happening at cathode during discharge cycle. Through this process, supply of unlimited quantity of free oxygen from atmosphere through porous cathode occurs and increases its capacity. This oxygen, which is vital for a secondary cell, is found in limited quantity encapsulated in the electrolyte medium in case of a metal-ion battery. In view of this, the capacity and energy density of MAB are quite higher than metal-ion battery. This is the reason why MAB is now the most preferred class of secondary energy storage device in important sectors of use like transport sector, space program, energy generators like wind turbines, photovoltaic panels, electric grids etc. apart from portable electronics and EVs. In an MAB, air cathode consists of porous carbon, a gas diffusion layer and electrocatalyst. Gas diffusion layer (GDL) enhances diffusion of oxygen between ambient air and catalyst surface. It has variable characteristics like lightweight, thin, highly porous, hydrophobic [17].

The anode of an MAB consists of a metal like Li, Na, Mg, Zn, Fe, Sn, K. The electrolyte may be aqueous, non-aqueous, solid-state, or hybrid type (combination of any two different solvents compatible with electrodes in use). For example, metals like Al, Zn, Fe, Sn are compatible with aqueous electrolyte, whereas metals like Li, Na, K are used with non-aqueous electrolyte [18].

Overall reaction scenario in an MAB is briefed as follows:

Cathode side: $O_2 + 2H_2O + 4e^- = 4OH^-$ (1)

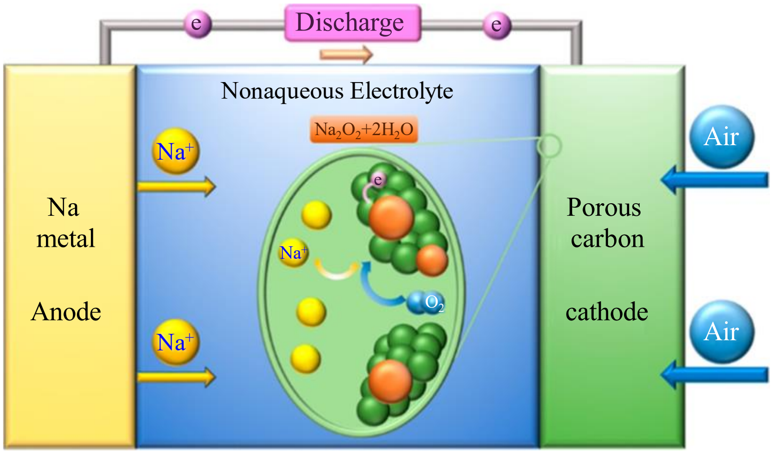

Figure 1. Functioning of a Na-air battery.

Anode side: M = M(n+) + ne$^-$ (2)

Transition of metal to metal-ions happens during discharge process and electrons are released and metallic ions are dissolved in electrolyte at anode. At the same time, oxygen from atmosphere passes through pores of cathode and hydro-oxides are formed. This moves in the electrolyte towards anode and combines with metallic ions and forms metallic hydro-oxide at the anode. Chemical activity of anode defines the discharge capacity of anode. These reactions out of chemical activity depend upon purity of metal, its thickness etc. The overall reaction continues to go on during discharge process and is reversed during charging. This operation continues till development high overpotential, formation of insoluble salts at cathode, formation of high passive layer on anode surface. Then, pore spaces are blocked and efficiency of the battery is reduced due to intermittent blockage of ion mobility in electrolyte and finally stopping its function. This is the dead end of the battery, when it needs to be disposed of and replaced [19–25].

In aqueous electrolyte, metallic electrode at anode is affected by corrosion, dendrite formation, passivation of metal-anode due to surface deposition of insulating metal-oxide film during discharge process. This reduces the efficiency of battery/termination of discharge process. But these problems can be resolved by using properly designed electrolyte additives along with taking a holistic approach to this. In case of non-aqueous electrolyte such as solid-state electrolyte, polymer electrolytes, etc; it helps in reducing leakage in electrolyte and increasing energy density.

Though, in non-aqueous category, Li-air battery (LAB) tops the list of MAB with highest practical energy density of 1700 Wh/kg and high cell potential (2.96 V), unit cost $68/kg, Na-air battery (NAB) comes next in the category with practical energy density of 1600 Wh/kg, cell potential of 2.27 V, lower unit cost of $1.7/kg, low dendrite formation, safer, etc. This is due to naturally availability of abundant quantity of Na metal as compared to others. Functioning of an NAB is shown in Figure 1.

LITERATURE REVIEW

Basics of an MAB is as follows: the constituents are its metal anode which releases electron externally and metal ions through electrolyte which then overcomes the separator barrier and mixes with the hydroxide at the cathode.

In the process, anode gets oxidized which leads to the reduction of the cathode. This flow of metal ions and frequent reduction of oxygen is influenced by the presence of impurities in the electrolyte and simultaneously affects the degree of OER (oxygen evolution reaction) and ORR (oxygen reduction reaction), which defines the capacity and efficiency of a battery. Imbalance between OER and ORR causes formation of dendrites of anode, which leads to subsequent reduction of life and efficiency of battery.

In the investigation [1], four groups of catalysts like (i) Pt and Pt-based alloys (Pt-Au nanoparticles), carbonaceous materials (grapheme nanosheets), transition-metal oxides (Mn-based spinels and perovskite) and inorganic/organic composites (metal macro cycle derivatives) have been chosen and effectiveness of their use as a catalyst for electrochemical reaction along with the optimal design of air-cathode have been presented. The MABs have successfully proved to have higher utility in terms of capacity, safety risk, weight, efficiency and degree of applications as compared to the similar MAB, but have a number of limitations. Authors have pointed out that regardless of the benefits of MAB, it has certain disadvantages like lack of stability of anode in atmospheric moisture, lack of clear analysis of catalysis effect, fall in efficiency due to higher difference between charging and discharging potential, choice of suitable electrolyte and cathode material in compatibility with anode, to name a few [2]. At the end, there is a comparative analysis of Li-, Mg-, and Al-air batteries with regard to their overall functioning with regard to important parameters like life cycle, rechargeability, generation of excess heat during discharge developing a runaway like situation, cost etc. and finally proposing suitable measures for their improvement. Though MABs proclaim to be better off than the metal-ion batteries on the basis of their capacity (energy and power density), cycle life, specific weight, efficiency, cost, safety, high application level such as military, medical, etc. against limited applications of metal-ion battery in some consumer goods, they suffer from some major limitations with regards to the choice of anode, electrolyte, separator, cathode and catalysts. Here, the authors have given a detailed review on these parameters and proposed their perspective view towards tangible solutions to above problems [3].

The authors in [4] have discussed about the functioning and various challenges faced by flexible MABs. As the name says, here much thrust has been given on the design of flexible components of a metal-air battery such as its metal anode, air cathode, flexible electrolytes to make the battery safe, sustainable, temperature resistant along with cost-effectiveness and maintaining high energy density and long-life cycle to make it the most practically use battery in future. In this type of battery, anode comprises of a thin metal sheet and cathode is made of very thin carbon nanosheets like carbon nanotube (CNT), graphene, carbon fibers in order to lower the weight of battery. The electrolyte is a solid-state electrolyte.

Authors have highlighted problems faced by the components of MABs (anode corrosion, dendrite formation, electrode wearing out, energy losses), cathode (choice of appropriate gas-diffusion layer, porous carbon, catalyst layer), electrolyte (use of an efficient electrolyte medium (aqueous/non-aqueous/hybrid)) for better transport of ions and electrons for a continuous ORR and OER of electrodes and finally proposed to use 3D printing and laser processing of components like anode, cathode, separator, catalysts etc. to improve the overall functionality [5].

Authors have proposed the use of fibrous materials manufactured from metal, metal oxide, and carbon to fit into various components of an MAB when their specific utility is concerned, thereby appreciably improving thermal safety, conductivity of ions and electrons, life cycle, rechargeability, environmental friendliness, battery efficacy, etc. These improvements are achieved owing to unique properties of the fibers such as large surface area to volume ratio (high aspect ratio), highly porous nature, which helps in enhancing ion adsorption, increasing number of energy storage points finally improving overall battery efficiency and durability [6].

Authors have reviewed the updated progress in the field of manufacturing of anode and cathode along with optimization techniques adopted to improve the operation of MAB [8]. Various challenges which are being faced in its commercialization and the ways to overcome the hurdles have been discussed. Here, the authors have presented the updated progress in the area of MAB and the challenges faced by these batteries [9]. The ways to overcome these challenges have also been explained so that these high-power, low-cost batteries can be fully commercialized in future. Besides, in conclusion, the authors have presented us with some facts, such as aluminum can be a proper choice for anode in MAB due to its high energy density, low weight, lower cost along with better recyclability. Though the aqueous electrolyte provides higher ionic conductivity, it suffers from various limitations of safety, leakage, which can be ruled out by use of non-aqueous electrolyte. They are preferred over flow MABs on the basis of safety, long operational life, low maintenance, no loss of charge during discharge cycle. Here, the authors have reviewed the existing system of MABs, their basic configuration, roles played by different components along with their limitations and have finally proposed suitable modifications for their improvement [10]. As the demand for higher capacity battery is growing day by day, the overall cost has also increased. Hence, there is a need to bring a balance between the total cost of battery versus its performance during its life time. Here, above aspect of finding optimal cost has been critically reviewed, which includes its capital cost of battery, power conversion cost that includes cost of inverter and packaging and other ancillaries like container and inverter controls, cost of balance of plants (which covers the cost of site wiring, interconnecting transformers, cost of routine maintenance of equipment) and provision for other unforeseen expenses linked with power system [11]. In addition to these costs, cost of construction and commissioning cost are to be added. Besides, the cost of recycling of battery needs to be taken care of for arriving at final cost implications.

Large number of research studies are going on globally to find solutions to meet the demand in the portable and wearable electronics sector, where flexible solid-state MABs have emerged as the leading material due to their higher energy density, long-term sustainability, and mechanical flexibility to name a few of its benefits. Here, the authors have reviewed innovative catalysts for cathode, use of high-performance solid state electrolytes and metal anodes and the challenges faced currently along with the proposals looking at future perspectives of flexible solid state MABs [12]. It is well-known that the most important activity in a MAB is the proper functioning of air-cathode, which helps in the substantial improvement of cell capacity, thus making this battery in demand in the recent days. But, inadequate oxygen reduction and evolution (ORR/OER) happens frequently due to multi-step electron and triple-phase mass transfer. To alleviate this issue, graphene-based electrocatalysts have been preferred for use in air-cathode owing to their properties of high electrical conductivity, high aspect ratio, good catalytic properties. Authors have given a detailed explanation on the morphological analysis of design of electrode and discussed on the latest researches on graphene-based materials as electrocatalysts and its suitability for enhancing the efficiency of MAB [3].

The most essential component of an EV is its battery. But, amongst all its limitations, thermal runaway is considered as the most critical and this problem is very serious in case of heavy class of EVs like trains, spacecraft, etc. Hence, it is quite essential to install efficient temperature control system, which will help to maintain temperature at a reasonable threshold level and cool the battery of the engine. Here, the authors have reviewed the present available BTMS (British Thermal Management System) technologies like natural air, forced air cooling, liquid cooling, mini-channel cooling etc. [14]. Finally, looking at the benefits and limitations of all these available systems, forced air cooling system has been proposed as this provides minimum maintenance, smooth integration to system and as a whole improves the economic factor. Apart from this, the authors have also realized that a direct liquid cooling system can also be useful for a good BTMS for its similar cooling performances. Another type of MAB, that is, aqueous MAB has recently been the interest of research of scientific community because of some of its prominent properties such as superior energy density, it being environment friendly, highly reliable. In spite of all these benefits, this battery fails to deliver discharge performance because of use of inadequate electrolytes.

The worldwide push for environmental decarbonization through a methodical shift away from high greenhouse gas emission systems has driven researchers to focus on enhancing energy storage systems, a significant contributor to the issue. Out of all components of an MAB, electrolyte plays a key role for overall performance of a battery including its safety, capacity, durability. It constitutes about 75% of total weight of a battery. Therefore, the economical design of a suitable battery electrolyte is crucial, and global research is underway to explore various cost-effective and lightweight novel electrolyte materials, including aqueous and non-aqueous options such as polymer membranes immersed in liquid electrolyte, gel-like electrolytes, and solid-state electrolytes. In their study, the authors identified and addressed current bottlenecks in MABs, offering potential solutions to mitigate these challenges [16].

Additionally, the authors conducted a review on the utilization of biomass waste as a substitute for carbon materials in MAB air-cathodes [17]. They analyzed various biomass synthesis methods, highlighting their shortcomings in achieving a material capable of effectively replacing carbon in the air cathode for MABs. Recognizing the hindrance to MAB commercialization due to the absence of a stable and active electrocatalyst, the authors proposed an active bifunctional electrocatalyst for improved performance. They suggested that biomass waste could be instrumental in creating a sustainable and cost-effective carbonaceous air cathode for MABs.

The synthesis of a carbon electrocatalyst from biomass involves intermediate processes such as pretreatments, carbonization, activation, and doping. These steps control the size and structure, ultimately enhancing the efficiency and stability of the final product. While this process is generally applicable to processing biomass waste, the authors emphasize the need for tailored synthesis methods for each specific type of biomass waste, considering its individual properties. The authors believe that this approach could serve as a promising substitute for MAB air-cathodes and advocate for further ongoing research in this direction [26].

In battery science, two essential prognostications are typically conducted: fault diagnosis and the estimation of remaining useful life. Prediction of remaining life of a storage cell is very much essential to determine the life cycle of the battery taking into consideration the maintenance works which can be evaluated using standard stochastic methods. The accuracy of these methods heavily depends on the volume of data collected for the purpose. Greater the volume, higher the accuracy of the final output. In case of a storage battery system, its performance starts to decline as the period of use progresses. In case of a Li-ion battery, as the number of cycles (i.e. charging and discharging) increases, it undergoes some irreversible chemical reactions inside it, resulting in the increase of internal resistance of battery. The capacity of battery degrades as duration of use increases and sometimes, this can cause safety problems. Various methods like model-based methods, data-driven based methods and data-model fusion –based methods are followed to estimate the remaining useful life of a storage cell. The authors here have analyzed the results obtained by these stochastic methods and efficacy of these method have been detailed [17]. In this paper, authors have thoroughly reviewed the functioning of Li-air MAB and made a comparative study of other promising MABs such as Zn-air, Mg-air, and Al-air batteries [19]. They have made a few observations on functioning of air cathode. Air-cathode mainly contains a porous carbon material with an electrocatalyst and a polymer binder. Functioning of pores in a carbon cathode is very important, but very often these pores are clogged and have little space to allow free air to pass. They have recommended to use air-electrode model with optimum pore size in the range of 2 to 50 nm. Besides, they have also suggested the electrolyte with faster diffusion, higher ionic conductivity, low viscosity, and use of gelled electrolyte to contain evaporation. Consequently, they have also proposed for the use of solid-state electrolytes and bifunctional catalysts for a balancing ORR/OER reactions and to use multiple advanced characterization techniques like transmission electron microscopy, X-ray diffraction, nuclear magnetic resonance spectroscopy, Raman spectroscopy, etc. for a clear knowledge of reaction mechanism in the cell.

In spite of their very high theoretical capacity, MABs fail to deliver to their full potential due to the lapses in multifunctional actions associated with its components. Here, these issues along with latest development in alkaline metal air batteries have been discussed in detail and further follow-up remedial actions have also been elaborated. The authors have emphasized to strengthen the air cathode by using a very thin, porous graphite nanosheets with adequacy of pores and impregnating them by using a good electrocatalyst. They have also discussed the suitability on use of sodium-air battery, which has a high potential to become a leader in this area due to its abundant availability, higher energy potential, but some problems like improving reversibility of electrode reactions and other key issues need to be addressed. At the end, the authors have proposed to carry out further research on the innovation of better materials in order to attain the charging time to be within half an hour, cycle life of more than 3000 and a cruising range of 500 km. In order to augment the discharge capacity of MABs, while authors have used graphene nano-sheets (GNS) as air- electrodes for Na-air battery replacing the traditionally used

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carbon membranes [22]. By this process, they have been able to achieve a discharge capacity as high as 9268 mA h g^{-1}, simultaneously minimizing the over- potential, which is one of the critical challenges in the design of Na-air battery. The result showed that with GNS air-cathode, 0.25 M $NaPF_6$/DME (sodium hexa-fluorophosphate/dimethoxy ethane) electrolyte solution and Na-anode, specific capacity achieved was 9268 mA h g^{-1} and with same electrolyte and using carbon –fiber , specific capacity obtained was far low, that is, 180 mA h g^{-1} and with use of thin carbon-film, capacity was better with a value of 2030 mA h g^{-1}, which shows supremacy of GNS over normal carbon fiber and carbon-film as air-cathode and can be a suitable replacement in the design of a high-capacity Na-air battery.

An MAB utilized a porous germanium anode with a hierarchically structured order achieved through controlled etching [23]. This configuration was tested for its potential in a high power density Ge-air battery, demonstrating stable and long-term durability across varying current levels. The findings revealed an energy density of 7.85 kWh/L for the germanium anode, as compared to 9.31 kWh/L for zinc and 6.96 kWh/L for lithium. This outcome suggests that germanium could serve as a viable alternative to zinc and lithium as an anode material in MABs, addressing urgent demand considerations In another experiment, CNT without any additives and binders were tried as catalyst for a Na-O_2 battery to evaluate its electrochemical potential. The result showed a very high discharge capacity of 7530 mA h g^{-1} and cyclic performance of 1000 mA h g^{-1}. Hence, the result is encouraging [24]. In order to increase the electrochemical activity of a Na-air battery, NCNT (nitrogen-doped carbon nanotubes) and pure/nascent CNTs were used as air-cathodes and observed highly reversible electrochemical reactions and higher capacities at low current densities [25]. It was felt that this higher result may be due to the self-stacked aligned NCNTs assisting in the transportation of large volume of oxygen along with liquid electrolyte. The morphological analysis showed uniformity in the coverage of discharge product in case of NCNT, whereas spread was quite random and non-uniform with CNT [27]. The authors suggested that this improved result may be due to higher catalytic activity of nitrogen-doped sites in NCNT.

The abundance, lower cost of Na metal along with its very high value energy density has put Na metal batteries at a competitive place. However, at room temperature, Na metal anode fails in providing good reversibility in electrochemical activity due to non-uniformity in the formation of solid electrolyte interphase (SEI) and dendrite formation. In order to resolve this issue, the authors have tried to use liquid electrolyte namely sodium hexa-fluorophosphate in mono/di and tetra/glyme forms, which showed high reversibility and non-dendritic plating-stripping of Na- metal anode [28]. The sustained and high reversibility observed in the electrolyte facilitated the creation of a consistent SEI comprising sodium oxide and sodium fluoride. This development is recognized as a crucial element for the advancement of future high-energy Na-air batteries.

At low temperature, Na metal loses majority of its reversibility property, thereby weakening its electrochemical activity. Artificial SEI was formed by plasma-enhanced atomic layer technology at a low temperature [29]. It was observed that an ultra-thin layer (2.8 nm) of Al_2O_3 coating helped in protecting the decomposition of electrolyte and preventing the 3D formation of dendrite thereby enhancing cycle, stability, high strength of a Na-metal battery.

Potentiality of Na-air battery has been discussed [30]. Recently, a lot of research is being carried out for Na-air battery which can be the most sought for battery in future owing to its properties like low cost, huge availability, energy efficiency, attaining high energy density (discharge capacity) of 9268 mA h/g at low current density of 500 mA/g and 1100 mA h/g at high current density of 100 mA/g, thus justifying its stability at both low and high current. But the formation of both NaO_2 and Na_2O_2 simultaneously as discharge product is still to be reasoned out, which indirectly lowers the efficiency of a Na-air battery. Research is being undertaken to contain the formation of NaO_2.

One significant drawback associated with Na-air batteries is the precipitation of discharge products (NaO_2/Na_2O_2/Na_2CO_3) on the air-cathode's surface, which consists of pure carbon without any catalyst.

This hinders the flow of free oxygen into the system, impeding proper electrolytic activity. Consequently, there is a need for a well-thought-out design of the air-cathode. A macro-homogeneous model of a non-aqueous Na-air battery was developed by substituting the conventional carbon air-cathode with a gas diffusion electrode and subsequently tested [31]. The results demonstrated a noteworthy 48% increase in discharge capacity compared to 1551 mA h/g (for carbon) at 0.1 mA/cm^2. This suggests the enhanced value of using this modified design in Na-air battery development.

Electrocatalysts with bifunctional and binder-free properties help in the development of a high-performance metal-air battery. Vanadium oxide (VO_2) nanostructure was used as an electrocatalyst for a rechargeable aqueous Na-air battery [32]. VO_2 was prepared on reduced graphene oxide (rGO) coated on a carbon paper and had a carambola morphology. This binder free VO_2 was used as air-cathode to design a Na-air cell and this cell was used for the experiment. This test showed that the cell had 0.64 overpotential gap, 104 mW g^{-1} power density at 80 mA g^{-1} current density, 81% overall efficiency and was stable for 50 cycles.

A metal-air battery runs with metal oxidation and oxygen reduction at air-cathode. Critical factors which normally influence the design are round-trip efficiency, flow of electrons in the circuit as well as ion-flow in electrolyte and adequate air-flow. Here, principles of design of these material components have been dealt with [33]. Final aim is to reduce the overpotential at air-cathode, maintaining a balanced gas diffusion in order to maintain a balance ORR and OER for a battery with higher efficiency in cycles, energy density and durable safe operation.

One of the critical factors of Na-air battery is proper design of its metal-anode, which fails to act when suffers from unstable plating / stripping actions. In order to solve this issue, the metal-anode of Na-air battery is modified with a super elastic graphene lattice in form of hierarchical structure fabricated by adopting 3D printing technique through direct inkjet writing. The modified design helped in regulation of the Na deposition on the rim regions and turning this region of holes, a zone for highly concentrated current density and thus, stabilizing the anode. This modification enhanced coulombic efficiency to as high as 99.84% for a long 500 life cycles, equivalent to 1000 hours of trouble-free functioning [34].

The basic problem of Na-anode in a Na-air battery is its decomposition. This being an essential component of Na-metal battery, plays a key role in overall functioning of storage cell. The metal-anode of the cell suffers from its degradation, formation of an unstable SEI promoting dendrite growth, poor coulombic efficiency. In order to solve this issue, a number of suggestions have been followed such as use of improved electrolytes by adding electrolyte additives fitting to a Na-metal battery, interfacial remedy at the interface of metal and electrolyte, modifying electrode architecture, use of solid-state electrolytes, polymer- based/gel-based electrolytes etc. [35]. Here, $SnCl_2$ is added to carbonate electrolyte to activate the instant reaction between $SnCl_2$ and Na metal leading to formation of Na-Sn alloy layer and a solid NaCl-rich SEI [36]. This helped in the quick transfer of interfacial ion, reducing formation of dendrite and enhancing cycle period to more than 500, thereby clearing ground for design of a high-performing Na-metal battery. Nickel-cobalt phosphide was used as an electrocatalyst for ORR/OER in MAB; however, its performance is characterized by a notably sluggish response. Here, the above compound is modulated with Fe dopants and when used in electrolyte, increases its conductivity in a hybrid Na-air battery as well as achievement of efficiency of 93.26% at 500th cycle and power density of 621 mW g^{-1}, which is quite satisfactory [37]. One of the serious concerns for a Na-metal battery is uncontrolled deposition of Na on the surface of metal anode, forming a dendrite like structure leading to problems like reduction in energy density, sluggish electrochemical reaction and also raises safety concerns. It is reported that by adjusting Na^+ flux near interface of electrolyte and electrode, and simultaneously by improving sodio-philicity on the bi-phase interface, homogeneous deposition of Na can be ensured [38]. In another similar experiment, a multistructural interphase layer made with sodium-fluoride SEI and Na_3Sb bars placed in a crisscrossed shape embedding Na electrode

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surface were used. The result showed improved interphase strength and Na^+ conductivity. Further, the experiment showed stable and dendrite free anode and found to be compatible with different cathodes giving excellent cycle performance of Na-metal battery [39]. In continuity towards further improvements of metal-anode to take care of problems like N-dendrite growth and uncontrolled volumetric expansion, a hybrid form of rGO/MXene film was prepared by filtration and spark process and used as a sodiophilic anode host to stabilize the metal-anode. The MXene sheets attached to its surface helped to regulate Na deposit and dendrite growth, while rGO scaffold helped in better electron transport system, thus provided an improved electrochemical action for Na-metal battery [40].

In another experiment, hierarchical mesoporous NiO nanosheets arrays prepared on carbon papers were synthesized by calcinations process and used to act as an integrated electrode for hybrid sodium-air batteries. The result showed increase in electron conductivity, provided high mechanical stability, increase in energy conversion efficiency by shortening ion transfer length, accelerating ORR/OER process. This modification helped also in excellent cyclability of 170(170 hr) at a low current density of 0.1mA cm^{-2}, and low overpotential of 0.65 V [41, 42].

Here, a brief review on research works in progress on air-cathode with reference to different materials use like pure carbon, CNT, carbon nanofiber (CNF), porous carbon spheres, graphene, rGO and porous carbon as cathode material have been made [43]. Similarly, on enhancement of electrochemical performance, transition-metal based electrocatalysts such as CoB, CoP, SnS_2, CoO, Co_3O_4, Mn_2O_3 etc. have also been discussed. Then, defect engineering has been considered to improve OER/ORR activities. Electrohemical behavior of a NaO_2 (sodium peroxide) battery was tested at room temperature and the report shown in [44] showed that the cell acted reversibly during both discharging/charging cycles at lower overpotentials of (<200 mV) and current densities of as high as 0.2 mA cm^{-2} with use of pure carbon cathode without a catalyst as compared to lithium-air cell, where irreversible reaction takes place. Rechargeable MAB is now very popular in the field of batteries owing to its very high theoretical energy densities and thus, can be a leader in storage energy sector because of the reduction in the consumption of oil. Here, Na-air battery was tested at a temperature above melting point of sodium [45]. The study reported on the formation of SEI along with its decomposition and the faradic efficiency of Na deposition and dissolution.

Key factor in an MAB is the functioning of air-cathode, the positive electrode. Here, study was conducted to find the kinetics and rechargeability of MAB [46]. Test was conducted with control surface area and porous structure of cathode and found that discharge capacity is linearly correlated with quantum of surface area of cathode. Morphological behavior heavily depends on specific surface area and size of pores on cathode. Besides, chemical composition of the discharge products and charging overpotential depend on rate of discharge reaction. In another test [47], $NiCo_2O_4$ nanosheets supported on Ni foam were used replacing pure carbon cathode in a non-aqueous Na-air battery and the result showed an initial discharge capacity of 1762 mA h/g with a low polarization of 0.96 V at 20 mA/g. Further, it showed only Na_2O_2 nanosheets as discharge material in place of normal NaO_2 as first discharge material and thus viewed that this will be a suitable material for air-cathode. In a test conducted [48] with use of Vulcan XC72R- coated and un-coated carbon paper as air-cathode in Na-air battery, the voltage efficiency were 78% and 72.4%, respectively, whereas with the use of Pt/C-coated carbon paper as air-cathode, the voltage efficiency was found to be 84.3% and a stable discharge voltage of 2.85 V, thus proving these catalysts to be suitable for stable design of Na-air battery. In reference [49], an ordered mesoporous carbon was created and applied as a nanostructured conductive framework within a Na-air battery. This framework served to accommodate less conductive byproducts generated during the discharge process. The electrolyte, based on carbonate, underwent decomposition, resulting in the production of Na_2CO_3. Furthermore, the cathode employing ordered mesoporous carbon (OMC) exhibited reversible formation and decomposition of Na_2CO_3. This characteristic led to a stable cyclic behavior with low polarization, sustained over 20 cycles at a capacity of 500 A h/g and a current density of 100 mA/g.

It is known that bi-functional catalysts are very useful to develop high capacity, higher energy efficiency, and have a long life-cycle when used in aqueous Na-air rechargeable batteries. Here, a bi-functional (ORR/OER) noble metal free $Co_3(PO_4)_2$ electrocatalyst was used as an air-cathode with a purpose to test the validity of use of a noble metal free air electrode for a rechargeable aqueous Na-air battery [50]. The result showed low overpotential (0.59 V), 83% round trip efficiency, good cyclic stability, which was found to be better off Li-air battery.

In the subsequent experiment [51], a test was conducted utilizing a dual-phase spinel, $MnCo_2O_4$, combined with nitrogen-doped rGO (dp-$MnCo_2O_4$/N-rGO), serving as a promising electrocatalyst. The outcome was highly promising, exhibiting commendable ORR and even superior OER performance compared to commercial Pt/C. Additionally, the hybrid demonstrated a low overpotential of 0.39 V, contributing to enhanced round-trip energy efficiency, excellent discharge stability, and minimal electrode degradation. These results highlight its potential utility in the design of a hybrid Na-air battery.

Here, the effect of contamination on NaO_2/Na_2O_2 by CO_2 to study various parameters like growth, depletion reaction pathway and formation of overpotential were studied for rechargeable non-aqueous Na-air battery [52]. Results showed an increase in the discharge electrochemical overpotential, hindering growth/depletion mechanism pathways drastically. Thus, it is advised to avoid CO_2 contamination released from electrolyte decomposition while designing Na-air battery.

The characterization of OER/ORR processes in Na-air battery was conducted by rotating disc electrodes (RDEs) and cyclic voltammetry (CV) methods with fresh and aged polyethylene glycol dimethyl ether 500 (PEGDME500)-based electrolyte. Result showed that oxidation overpotentials of the reduced products were much dependent on the time of storage of this electrolyte [53]. This change starts from the synthesis process, when sodium alchoholate molecule remain in the electrolyte. Aging of PEGDME500 is prevented by the insertion of metallic sodium. The result further indicated that Na_2O_2 is main end product of tetraethylene glycol dimethyl ether (TEGDME).

REVIEW OF RESEARCH WORKS (2012–2023)

Various studies have been elaborated and shown in Table 1. Normal Na-O_2 battery uses nonaqueous solvents and releases insoluble discharge products of NaO_2 and Na_2O_2, leading to very high overpotential gap, poor cyclic stability, where as a hybrid Na-air battery releases soluble discharge product in form of NaOH, leading to low overpotential gap and good cyclic stability and reasonable safety. Authors have concluded that hybrid Na-air batteries are better as compared to NaO_2 batteries, but cautioned about its large-scale use as this technology is still at a very early stage of development [54].

Table 1. Review of research works.

Battery component	Author(s)/ year	Challenges	Remedial measures proposed	Experiment/ theoretical
MAB (complete metal-air battery)	Cheng, F. et al. (2012)	Design of electro-chemical catalyst for air-cathode	Four groups of catalyst chosen and tested for functional effectivity.	Experimental analysis
	Rahman, M, A. et al. (2013)	Limitations of metal-air battery	Limitations identified, a comparative analysis of Li, Mg, Al-air batteries done and suitable measures proposed	Theoretical analysis
	Yanguang, L. et al. (2017)	Drawbacks of metal-air battery and its solution	Review of these parameters and tangible solutions reported.	Theoretical analysis
	Qingchao, L. et al. (2017)	Design of components of flexible MAB for sustainability of a MAB	*Anode:* thin metal sheet. *Cathode:* carbon fiber, graphene, CNT solid-state electrolyte	Experimental analysis
	Wang, C. et al. (2019)	Inherent problems of MAB and its mitigation by adopting suitable design of components.	Design of appropriate GDL (gas diffusion layer), choice of electrolyte (aqueous/nonaqueous/hybrid) and use of 3D/laser printing of anode, cathode, separator.	Experimental/ theoretical

Battery component	Author(s)/ year	Challenges	Remedial measures proposed	Experiment/ theoretical
	Xiaoqing, C. et al. (2020)	Improving thermal safety, conductivity of ions and electrons, increase in energy storage of MAB	Use of fibrous materials manufactured from metal, metal-oxide, carbon in components of MAB	Experimental analysis
	Concetta, S. et al. (2021)	Sustainability issues and commercialization of MAB, use in desalination and waste water treatment and remove hurdles in its commercialization.	Adoption of optimization techniques to improve operation of MAB and application process in desalinating waste water.	Experimental/ theoretical
MAB (complete metal-air battery)	Olabi, a, g. et al. (2021)	Mitigation of various deficiencies in MAB with focus on achieving higher energy density, efficiency.	Gradual transition from traditional voltaic cell to MAB with advanced flow-technologies for better safety, low maintenance, long operational life.	Theoretical
	Mongird, K. et al. (2020)	Evaluation of energy storage cost and performance characteristics	Cost versus performance parameters of 6 (BESS) and 4 (non-BESS) battery energy storage systems along with their annualized cost compared and prioritization of battery reported. Total cost included capital cost of battery, power conversion system, balance of plant, cost of construction and commissioning and O&M cost.	Theoretical analysis
	Ning, L. et al. (2022)	A promising portable energy storage device with high capacity, durability and mechanical flexibility: Flexible solid-state MAB.	Detailing of working principle, design, challenges and future perspectives (in testing stage)	Theoretical
Electrolytes and electrocatalyst	Deng, J. et al. (2022)	Validating roles of graphene in electrocatalyst of MAB to accelerate ionic and electron conductivity, efficiency, sustainability	1st, requirement of efficient oxygen for electrocatalyst was determined. 2nd, quantum of graphene was estimated to be used in design of electrocatalyst.	Experimental analysis
Total battery	Arvind, B. et al. (2022)	Efficient ways of thermal management of an EV battery	Adoption of efficient cooling systems like forced air cooling, liquid (direct/ indirect) cooling and mini channel cooling have been tested and compared. Forced air cooling system has been found to most beneficial out of above 4 systems.	Experimental analysis
Electrolyte	Linqian, W. et al. (2022)	Issues before MABs, (Al, Fe, Mg) are analyzed.	• Design of novel anode • Adoption of functionalized electrolyte, acidic electrolyte • Efficient air-cathode	Theoretical analysis
Electrolyte	Manuel, S. et al (2022)	Challenges and environmental issues of MAB	• Mixing FDMH with DME in electrolyte to provide oxidation stability and enhance ionic conductivity. • By pre-fixing CO_2 in PVA electrolyte to avoid poisoning effect of CO_2 in atmosphere.	Theoretical review
Electrode	Lim, B. A. et al (2023)	Use of bio-mass waste in energy storge applications	Carbon materials were produced from biomass-waste by synthesis method for use as air-cathode tailored to need of different MAB to reduce unit cost.	Experimental

Battery component	Author(s)/ year	Challenges	Remedial measures proposed	Experiment/ theoretical
MAB (complete metal-air battery)	Liyan, S. et al. (2023)	Prediction of useful life of energy storage system	Broadly categorized into 3 types of methods: (1) Model-based methods, (2) data-driven methods and (3) data-model-fusion based methods	Review paper, theoretical
Electrodes	Liu, W. et al. (2013)	Design of air electrode for a Na-air battery for enhanced electrochemical performance	GNS (graphene nano sheets) were used as air-cathode for Na-air battery and showed high discharge capacity as high as 9268 mA h g^{-1} with low overpotential and showed its edge over normal carbon film electrode.	Experimental
Electrodes	Ocon, J. D. et al. (2013)	Design of anode of a MAB	Synthesis of porous germanium to form an ordered hierarchical structure to act as anode of MAB and result was encouraging.	Experimental
Electrodes	Zelang, J. et al (2014)	Design of air-cathode of MAB	CNT paper was used directly as catalyst in cathode without any additive and binder. Result showed a high discharge capacity of 7530 mA h g^{-1}, which was highest as on date with improved capacity of 1000 mA h g^{-1} and overall potential gap of very small 200 mV.	Experimental
Electrode	Qian, S. et al.(2015)	Design of a long-life air-electrode for Na-air battery	Nitrogen-doped CNT (NCNT) and pure CNT were used as air-cathode in Na-air battery and tested Test result showed that NCNT have higher capacity under high current as compared to CNT. It may be due to robust alignment NCNT enabling rapid oxygen and liquid electrolyte transport.	Experimental
Electrode	Seh, Z. et al. (2014)	Deign of reversible sodium metal anode at room temperature	Na–metal at room temperature suffers from demerits like poor reversibility during long-term plating and stripping due to formation of SEI and dendrite growth. When sodium-hexafluoro-phosphate in glymes is used as electrolyte in Na-air battery, it showed higher reversibility and non-dendrite formation with high coulombic efficiency of 99.9% at 0.5mA cm^{-2}.	Experimental
Electrode	Luo, W. et al. (2016)	Design of stable sodium metal anode	Using an ultra-thin layer of Al_2O_3 (2.8 nm thick) plating over Na-metal anode helps in formation of artificial layer of SEI, thereby protecting Na metal from electrolyte decomposition, dendrite formation along with increasing cycle stability.	Experimental
Electrode	Sahapatsombut, U. et al. (2016)	Modelling of rechargeable Na-air battery with porous gas diffusion electrode.	By replacing conventional flooded electrode(carbon) with a porous gas diffusion electrode, initial discharge capacity of a Na-air battery increased by 48% (1551 mA h g^{-1} at 0.1 mA/cm^2, showing a promising performance.	Experimental

Battery component	Author(s)/ year	Challenges	Remedial measures proposed	Experiment/ theoretical
Electrode	Ziyauddin, K. et al. (2017)	Design of binder free air-electrode for an aqueous Na-air battery	VO_2 (vanadium oxide) nanostructure was prepared on rGO coated on a carbon paper having carambola shape and used as air-cathode in a rechargeable Na-air battery and showed 81% round-trip efficiency, stability up to 50 cycles at 80 mA g^{-1} current density.	Experimental
Electrode	Yikang, Y. et al. (2019)	Design of advanced Na metal anode	Superplastic graphene lattice (GL) with hierarchical structure was fabricated using 3D technique and used as metal- electrode. The rims of pores showed high current density and served as sites for Na deposition and formed a Na metal anode and stood for 500 cycles and coulombic efficiency of 99.84% at a current density of 1 mA cm^{-2}	Experimental
Electrocatalyst	Yao, K. et al. (2020)	Boosting of power density of hybrid Na-air battery.	Nickel cobalt phosphide functions as potential electrocatalyst for ORR/OER. Here, iron doped (Fe-NiCoP) embedded in amorphous carbon layer catalyst on nickel foam was used as air-electrode and gave 93.26% round trip efficiency of 500 cycles, discharge voltage of 2.74 V at 0.01 Ma cm^{-2}	Experimental
Electrode	Xianming, X. et al. (2021)	Design of electrodes for high energy Na-metal battery	One of the main drawbacks of rechargeable Na-metal battery is non-uniform dendrite formation on surface of metal electrode. Na-electrode is designed for a uniform deposition of dendrites thereby maintaining adequate capacity.	Theoretical review
Electrode	Shiyong, W. et al. (2021)	Novel design of anode in a Na-metal battery.	Na-metal anode is modified by attaching a hybrid rGO/MXene film to its surface by filtration and spark process, which helped in regulating Na deposition behavior and control dendrite growth with excellent coulombic efficiency and long term cycling.	Experimental
Electrode	Wenhui, N. et al. (2023)	Design of integrated electrode for hybrid Na-air battery	Hierarchical mesoporous NiO nanosheet were grown on a carbon paper and synthesized and used as an integrated cathode for HSAB. Test showed improvement in OER/ORR, low overpotential of 0.65V, power density 7.53 mW cm^{-2} and as high as 170 cycles.	Experimental
Electrode	Pengcheng, M. et al. (2023)	Comprehensive review of cathode materials for Na-air batteries		Theoretical
Electrode	Liu, W.-M. et al. (2014)	Design of electrodes of non-aqueous Na-air batteries	$NiCo_2O_4$ nanosheets/Ni electrode when used in design of non-aqueous Na-air battery are highly efficient with initial discharge capacity of 1762 mA h g^{-1}, overpotential of 0.96 V at current density of 20 mA g^{-1} and found to be economic.	Experimental

Battery component	Author(s)/ year	Challenges	Remedial measures proposed	Experiment/ theoretical
Electrode	Sahgong, H.S. et al (2015)	Improving voltage efficiency of Na-air battery	Air-cathode of Na-air battery was coated with Pt/C and Vulcan XC72R and tested for its electrochemical properties. Test showed Pt/C coated air-cathode having 84.3% as compared to Vulcan coated 78% and 72.4% for un-coated carbon paper. Thus, Pt/C coated gave better result.	Experimental
Electrode	Won-Jin, K. et al. (2015)	Testing of nano-confinement of low-conductivity products in Na-air battery to decompose discharge output.	Ordered mesoporous carbon(OMC) was synthesized to form nano-structured conductive matrix ,which used in cathode helped in reversible formation and decomposition of Na_2CO_3 , thereby providing stable cycles with low polarization for 20 cycles with capacity of 500mAh/g at current density of 100Ma/g.	Experimental
Electrode	Senthilkumar, B. et al. (2016)	Cobalt-phosphate as a catalyst for Na-air battery	$Co_3(PO_4)_2$ was synthesized to form grain-like nanostructure and used in air-cathode and showed better catalytic behavior than Pt/C with a higher round trip efficiency and 50 stable cycles.	Experimental
Electrode	Kang, Y. et al. (2017)	Novel design of air-cathode with use of rGO in Na-air battery.	Dual-phase spinel cobalt manganese with nitrogen –doped rGO hybrid (dp-$MnCo_2O_4$/N-rGO) was used as catalyst in air-cathode of Na-air battery and showed better result with higher discharge voltage and lower charge voltage as compared to Pt/C, with a lower over potential of 0.39 V and 25 cycles.	Experimental
Electrolyte	Debora, R.M. et al. (2017)	Development of novel inorganic electrolyte for Na metal battery.	Highly concentrated inorganic electrolyte prepared by mixing sodium salt with liquid ammonia and result showed properties like low flammability, high specific conductivity, no dendrite formation, which were encouraging.	Experimental
MAB (complete metal-air battery)	Cai, T. et al. (2020)	ISC detection methodology in Li-ion storage battery	In a battery made of multiple cells, conventional method of internal short circuit detection does not work. For this, measurement of cell expansion force caused due to cell swelling is considered and analyzed for correct detection.	Experimental and analytical
Electrolyte	Barpanda, P. et al. (2021)	Design of efficient electrolyte for hybrid Na battery.	Homogeneous, carbon-coated, and spherical $K_2Co(PO_3)_4$, when used in hybrid Na-air batteries, produced reversible cycling efficiency over 70% by superior OER at low overpotential of 0.32 V.	Experimental
Electrolyte	Xianming, X. et al. (2023)	Design of multi-functional interphase layer for a superior Na metal battery.	By using an artificial heterogenous interphase comprising of (Na_2Se and (V) metal vanadium), there was homogeneous deposition of Na without dendrites. This gave outstanding cycling lifespan exceeding 1790 h in carbonate-based electrolyte.	Experimental

Internal short circuiting is a very critical issue for a storage cell leading to thermal runaway and explosion. Earlier method of detection was based on voltage/current measurement, which works properly for a single cell, but for battery with large capacity, it gives poor result. Another method proposed that includes measurement of expansion force, which is developed inside battery due to rise in temperature and side reactions, producing huge gases leading to swelling of battery [55]. The authors here have recommended the use of combination of voltage and expansion force for early detection of internal short circuit (ISC), which will be better and safe as compared to earlier methodology and recommended for further research into its refinement.

It is essential to design in efficient bifunctional electrocatalysts for ideal functioning of rechargeable hybrid metal-air battery. Here, homogeneous, carbon coated and spherical shaped cobalt based tetraphosphate ($K_2Co(PO_3)_4$) was used as an economic bifunctional electrocatalysts to act as cathode for rechargeable hybrid Na-air battery [56]. Result showed reversible cycling with round-trip efficiency over 70%, superior oxygen evolution with low overpotential of 0.32 V, which prompted the authors to recommend it for design of rechargeable, low-cost hybrid Na-air batteries.

With an aim to switch over from fossil fuel based to renewable energy sources, here [57], the authors have tested the use of polymer electrolytes as they have higher mechanical, thermal, and physicochemical properties along with safety, cost effective and adaptable. Besides, due to their easiness to blending, they can be tailored for various needs by adopting suitable blending methodology and can be developed further for design of proper energy storage devices.

COMPARISON OF COST AND ENERGY DENSITY OF DIFFERENT METAL-AIR BATTERIES

Comparison of cost and energy density of different MABs is shown in Table 2.

ANALYSIS OF REVIEW

To address the contemporary demand for high-capacity energy storage, MABs are now favored over metal-ion batteries (MIBs). While the initial focus was on lithium-ion technology, attention shifted to lithium-air due to its potential to overcome challenges such as low energy density, safety issues, extended cycling, and higher unit costs. The surge in demand for secondary sources has raised concerns about the depletion of lithium metal. Consequently, there is ongoing global research on sodium-metal due to its comparable energy density, natural abundance, reduced cost, improved safety, lower weight, minimal dendrite formation, higher ionic conductivity, and above all environmental friendliness and sustainable green energy.

In spite of above benefits, sodium-air batteries encounter challenges such as sluggish ORR and OER at the cathode, deposition of insoluble salts (Na_2O_2/NaO_2) blocking cathode pores, passivation of the metal anode, low cycling efficiency, dendrite formation, and reduced energy conversion efficiency and capacity.

Table 2. Cost versus energy density of different metal-air batteries.

Type	Calculated open circuit voltage (OCV) (V)	Practical energy density (W h/kg)	Metal cost ($/kg)	Efficiency (discharge), %	Capacity density (mA h/g)	References
Fe/Air	1.28	50–75	0.4	96	300–786	[52]
Zn/Air	1.65	350–500	1.85	-	300–875	[53, 58]
Mg/Air	2.93	400–700	2.75	-	737−2131	[30]
Al/Air	2.71	300–500	1.75	70	260–2777	[33, 58, 59]
Na/Air	2.27	1600	1.7	-	-	[60]
Li/Air	2.96	1700	68	68–94	3842	[58–61]
Sn/Air	0.95	-	21	70–90	-	[60, 62]

From preceding research data, it is observed that maximum research works are on electrodes, followed by on overall battery system and third on electrolyte and fourth on electrocatalysts.

Recommendations

To address these issues and bringing better functional system to MAB, extensive research focuses on various parameters as outlined in preceding para. Some of them are as detailed below:

1. *Design of a perfect metal anode*
   i. Use of thin metal sheets and doping with graphene to increase surface area and mitigate decomposition along with increasing sustainability.
   ii. Utilization of synthesized porous germanium for hierarchical anode structures.
   iii. Application of an ultra-thin layer of Al_2O_3 plating over sodium-metal anodes to form an artificial SEI and prevent decomposition.
   iv. Adoption of super-plastic graphene lattice with a hierarchical structure to enhance efficiency and cycling.
2. *Design of an efficient air cathode*
   i. Use of 3D and spray printing techniques for novel cathode design.
   ii. Synthesis of carbon materials from biomass waste for decarbonization and cost reduction.
   iii. Incorporation of graphene nano-sheets/CNT paper in the air cathode to accelerate discharge processes.
   iv. Application of various catalysts, including Pt/C, hierarchical mesoporous NiO nanosheets, carbon-coated $K_2Co(PO_3)_4$, nitrogen-doped CNT, and vanadium oxide nanostructures.
3. *Design of electrolyte and electrocatalyst*
   i. Deployment of efficient hybrid electrolytes, ionic-liquid electrolytes, and functionalized electrolytes.
   ii. Use of graphene and other catalysts to enhance ionic and electron conductivity.
   iii. Exploration of spinel oxides and highly concentrated inorganic electrolytes for improved safety and conductivity.

CONCLUSION

In conclusion, while each component of a sodium-air battery influences its performance, the primary challenges are linked to the air cathode and electrolyte. Effective bi-functional catalysts are crucial, and ongoing research aims to understand internal reaction mechanisms within the electrolyte system. Additionally, research should focus on designing anodes from vegetative wastes to create greener batteries and reduce the use of natural metals. The reviewed research indicates a lack of balanced attention to all cell components, highlighting the need for equitable research efforts. Furthermore, strict regulation and enforcement of recycling and reusing waste materials are essential to minimize environmental pollution. Proper guidelines for packaging, transportation, installation, and maintenance must be established and followed. A holistic approach involving manufacturers, end-users, regulatory authorities, and public awareness is necessary to enhance the reliability, safety, capacity, and cost-effectiveness of sodium-air batteries, positioning them as a leading sustainable energy storage solution for future applications.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Contribution

- The first author, Mitasha Swain, has full contributions like bringing idea, total writing, proof-reading, collecting and arranging all journal articles mentioned in the reference list.
- The second author (co-author) has discussed the shortcomings as and when approached by the first author during this work and advised as necessitated.

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