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Progress on Next generation Electrochemical Energy Storages: Status and Challenges

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Abstract: Transportation is the primary consumer of oil, accounting for a significant portion of global energy consumption (34%) and CO_2 emissions (40%). Electrifying road transportation is crucial to mitigate the effects of global warming. The abundant potential of renewable energy sources like solar and wind is hindered by their intermittent nature and incongruity with peak energy demands. This calls for the development of sophisticated energy storage solutions. Metal-air batteries (MABs), emerging as viable alternatives to lithium-ion batteries (LIBs), have attracted considerable attention due to their promising applications in the transportation sector. Despite substantial progress in MAB development over the past two decades, overcoming critical challenges such as electrolyte decomposition, carbon cathode degradation, anodic dendrite growth, and air impurities remains essential for their commercial viability. This mini-review provides a comprehensive overview of MAB fundamentals and the challenges associated with their development. The insights presented in this review serve to illuminate the current landscape and future prospects of MABs in the transportation sector.

Keywords: Li-ion batteries; higher energy density; metal-air batteries; renewable energy; transportation

1. Introduction

1.1. Renewable and Sustainable Energy

Energy plays a pivotal role in propelling economic growth across agriculture, industries, and service sectors. Despite the growing emphasis on renewable energy sources, fossil fuels remain the dominant players in the global energy landscape. The combined contribution of oil, coal, and natural gas makes up approximately 80% of the world's energy usage. These fossil fuel-based systems face several drawbacks: (i) their finite nature, (ii) their depletion rate exceeding their replenishment rate, and (iii) their detrimental environmental impacts. Driven by an annual growth rate of 2.3%, global energy consumption has witnessed a significant rise, primarily met by increased consumption of fossil fuels [1–3].

Climate change looms as one of the most pressing challenges facing our planet today. A significant portion of this crisis stems from the rampant consumption of fossil fuels across various sectors. Introduced during the industrial revolution, fossil fuels have driven the alarming accumulation of heat-trapping greenhouse gases (GHG) in the atmosphere. The 10 $GtCO_2eq$ surge in annual anthropogenic GHG emissions observed in the past decade (2001-2010) was primarily driven by the non-renewable energy sector, which accounted for 47% of the increase. Industry, transport, and buildings contributed 30%, 11%, and 3%, respectively [1]. Since 1970, industrial activities and fossil fuel combustion have been responsible for over three-quarters of the surge in GHG emissions. The compounding effects of GHG emissions on global climate change are expected to have irreversible consequences for agriculture, the healthcare sector, and the Earth's ecosystem as a whole [1,4,5].

The urgency to harness renewable energy sources and curb fossil fuel consumption has intensified in recent years [6,7]. Sustainable energy surpasses mere renewable energy by emphasizing energy efficiency. Optimizing energy supply to minimize wastage enhances energy efficiency [4]. Intertwining renewable energy sources and energy efficiency strategies forms the foundation of a sustainable energy paradigm, fostering economic progress, human well-being, and environmental protection. Sustainable energy solutions address climate change by reducing GHG emissions, ensure equitable energy access for all, and strengthen energy security [4]. The proportion of renewable energy in the global energy mix is on an upward trajectory. In the year 2017, renewable energy sources represented 18.1% of global energy production, with modern renewables contributing around 10.6%, and the remaining portion sourced from traditional biomass (refer to Figure 1) [5]. Utilizing currently available technologies, it is anticipated that the global proportion of renewable energy will surpass 30% by the year 2030 [8].

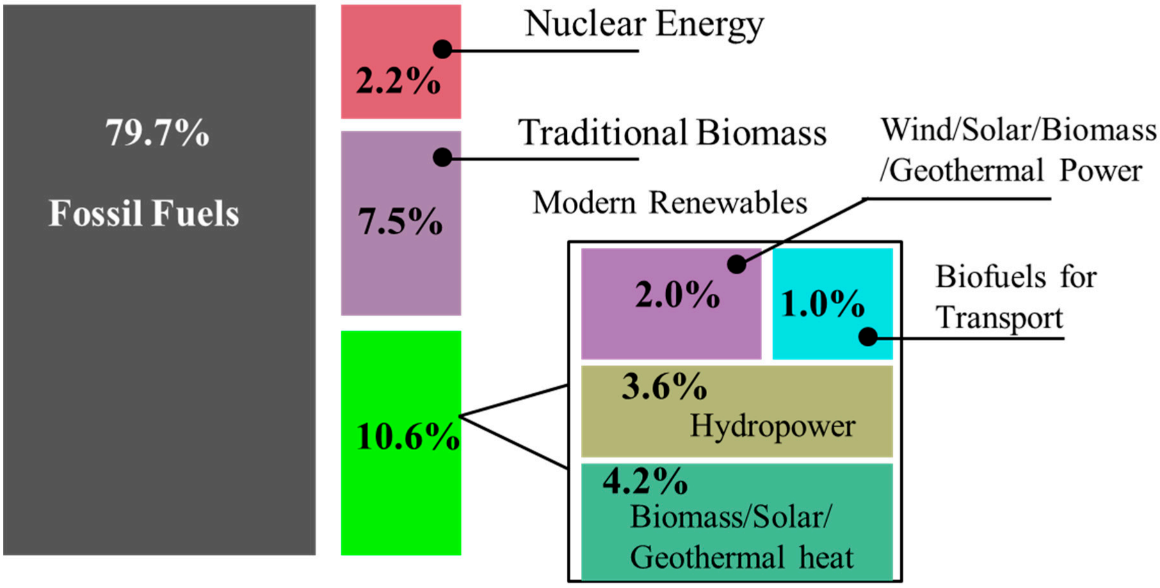

Figure 1. Proportion of renewable energy sources in global energy consumption for 2017 [5].

Renewable energy sources like solar and wind power are not always available, and their peak supply doesn't necessarily align with peak demand [1,9]. This intermittent nature necessitates the use of rechargeable batteries as backup energy storage during power fluctuations. Technological advancements have driven the demand for higher-performance batteries. The consumer electronics industry currently dominates the battery market, with LIBs holding a prominent position [10]. However, LIBs have seen only marginal improvements in price and efficiency since their commercialization in 1991 [10–12]. Therefore, novel developments are crucial to enhance battery reliability, safety, energy/power density, and reduce battery costs per kWh of energy storage.

1.2. Battery Technologies

Batteries, also known as electrochemical cells, are devices that harness chemical energy and transform it into electrical energy. Alessandro Volta pioneered the development of the first electrochemical battery in 1800, featuring copper and zinc electrodes submerged in a saltwater (NaCl solution)-soaked paper electrolyte. The year 1836 saw the introduction of the Daniell cell by John Frederic Daniell, a crucial milestone that set the stage for contemporary battery technologies. Subsequently, battery technology has experienced notable progress. Batteries can be broadly categorized into two types: primary and secondary. Primary batteries are designed for single use and cannot undergo recharging. In contrast, secondary batteries, also known as rechargeable batteries, are capable of being recharged and discharged repeatedly [2,11].

Gaston Planté's breakthrough in 1859 with the lead-acid battery paved the way for rechargeable batteries. It utilizes lead and sulfuric acid to store and release energy [13]. Lead-acid batteries are known for their ability to handle high current loads and their suitability for both accessory batteries and power sources in cars. They are relatively inexpensive, reliable, and easily recyclable at the end of their lifespan. However, their disadvantage lies in their weight and bulkiness relative to their energy storage capacity. Nickel-cadmium (Ni-Cd) rechargeable batteries, pioneers of alkaline technology, were commercialized in the late 19th century. These batteries utilize nickel and cadmium electrodes immersed in a potassium hydroxide electrolyte. Ni-Cd batteries boast higher energy densities (60-100 Wh/L) than lead-acid batteries (50-80 Wh/L) [11].

Emerging in 1989, the nickel-metal hydride (Ni-MH) battery employs a positive electrode of nickel oxyhydroxide (NiOOH) similar to Ni-Cd batteries but utilizes a metal hydride instead of cadmium for the anode material. Ni-MH batteries offer superior energy densities (170-430 Wh/L) and are environmentally preferable due to the absence of toxic cadmium electrodes (Figure 2). These batteries have gained widespread adoption in mobile devices, electric vehicles, and hybrid electric vehicles. However, their high cost and heat generation at high current draws remain challenges for this technology [11].

The debut of rechargeable LIBs by Sony in 1991 signified a crucial milestone in battery technology [11]. Initially, graphite served as the anode material, while $LiCoO_2$ was employed as the cathode (Figure 2). Graphite has since established itself as the preferred anode material due to its favorable properties, including safety, reversibility, and the ability to deliver high energy density for portable electronic devices. However, the widespread use of $LiCoO_2$ has been met with concerns regarding its high cost, toxicity, and safety limitations. To address these issues, alternative cathode materials, such as lithium iron phosphate ($LiFePO_4$), manganese spinels, and lithium nickel manganese cobalt oxides, are actively being explored [11].

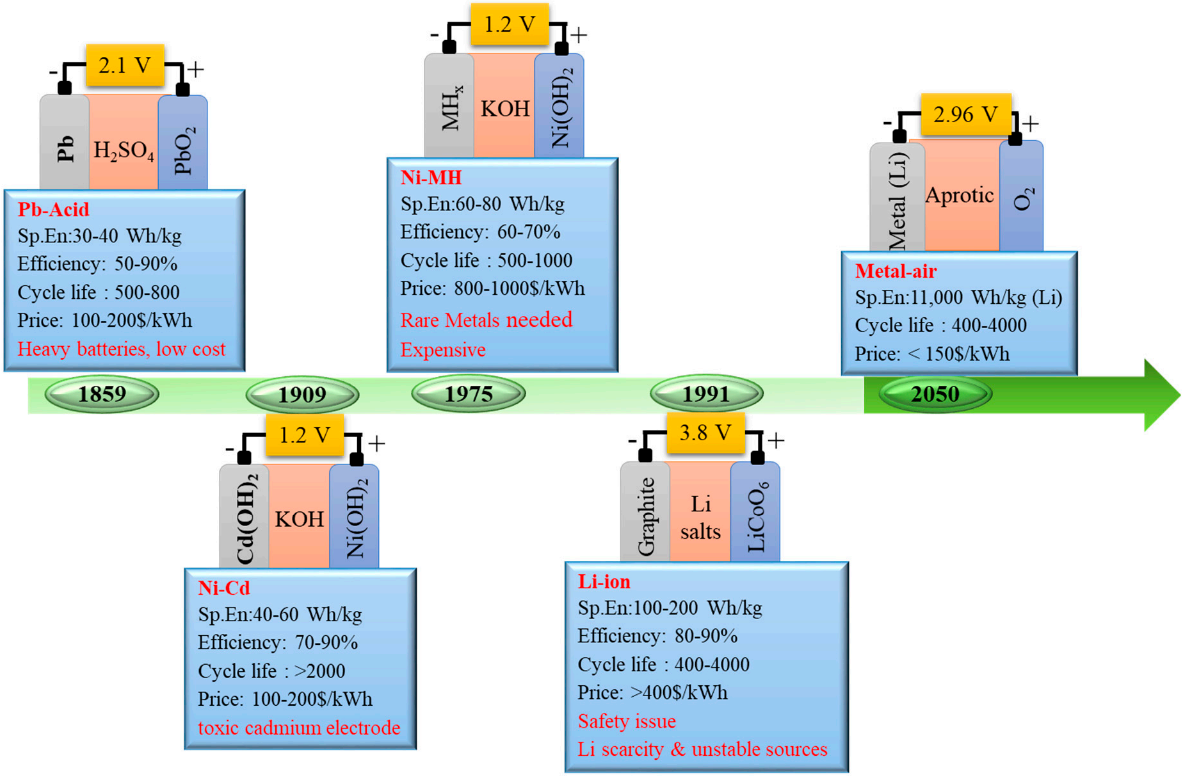

Figure 2. Evolution of rechargeable battery technologies over time (Adopted from ref. 9).

LIBs are rapidly gaining prominence as a versatile energy storage solution, catering to a diverse spectrum of devices ranging from compact appliances like watches and hearing aids to extensive applications like grid-scale energy storage systems and electric vehicles. To understand the operation of LIBs, it's essential to grasp the fundamental principles of battery technology. At the heart of any battery lie three key components: two electrodes, the cathode and anode, separated by a porous barrier called the separator, and an electrolyte solution. Figure 3 illustrates the working mechanism of LIBs. The electrodes are composed of two distinct materials, separated by the separator. During discharge, a chemical reaction occurs between the electrodes, releasing electrons in the form of electricity. This reaction is facilitated by the electrolyte solution, which allows ions to flow between the electrodes. The electrolyte solution must be designed to conduct ions efficiently while preventing the flow of electrons. As the anode undergoes a chemical reaction, it releases electrons at the battery's negative terminal. These electrons travel through the external circuit, powering the connected device. Simultaneously, ions migrate through the electrolyte solution towards the cathode [11]. At the cathode, these ions unite with electrons, giving rise to compounds that accrue on the surface of the cathode [11]. This process is reversed during charging, where an external energy source drives the flow of electrons back into the battery, reversing the chemical reactions and restoring the initial state of the electrodes. The chemistry of LIBs revolves around the movement of lithium ions (Li+) within the battery. During charging, Li+ ions intercalate into the negative electrode, typically graphite, and during discharge, they react with Li+ ions at the positive electrode, where materials like $LiCoO_2$, $LiMn_2O_4$, or $LiFeO_4$ are commonly used [11].

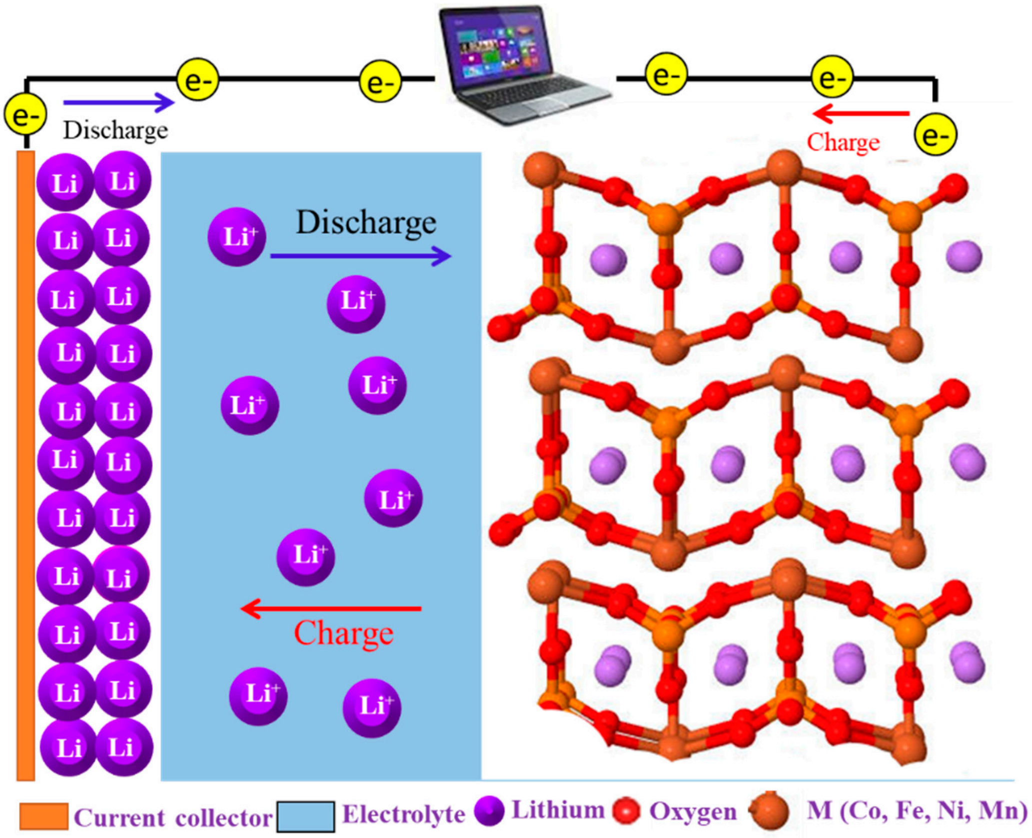

Figure 3. The operational principles of a LIB (Adopted from ref. 10).

Electrifying vehicles with high-capacity rechargeable batteries has gained significant attention as a means to reduce or eliminate the reliance on internal combustion engines. In the realm of battery technologies, rechargeable lithium-air batteries have garnered attention as a promising alternative, exhibiting an exceptional energy density comparable to that of gasoline. While LIBs currently power most electric and hybrid electric vehicles (HEVs), their limited range and high cost pose challenges for widespread adoption. Affordable electric vehicles typically offer a driving range of around 120 miles, while luxury EVs like the Tesla S can reach up to 270 miles but come with a hefty price tag of nearly $100,000 [14]. Therefore, the development and implementation of safe, long-lasting, and cost-effective rechargeable batteries are crucial to meet the growing energy storage demands for various applications. The present accessible rechargeable LIB capacity is too limited to address these demands [15]. This comprehensive review delves into the emerging field of MABs, a promising renewable energy technology that holds the potential to revolutionize energy storage solutions. Characterized by their exceptional theoretical specific energy, surpassing that of other battery types (Figure 4) [15–17], MABs, particularly Li-O_2 and Na-O_2 batteries (SOBs), offer the tantalizing prospect of powering vehicles for distances comparable to those achieved with fossil-fuel-based counterparts [18].

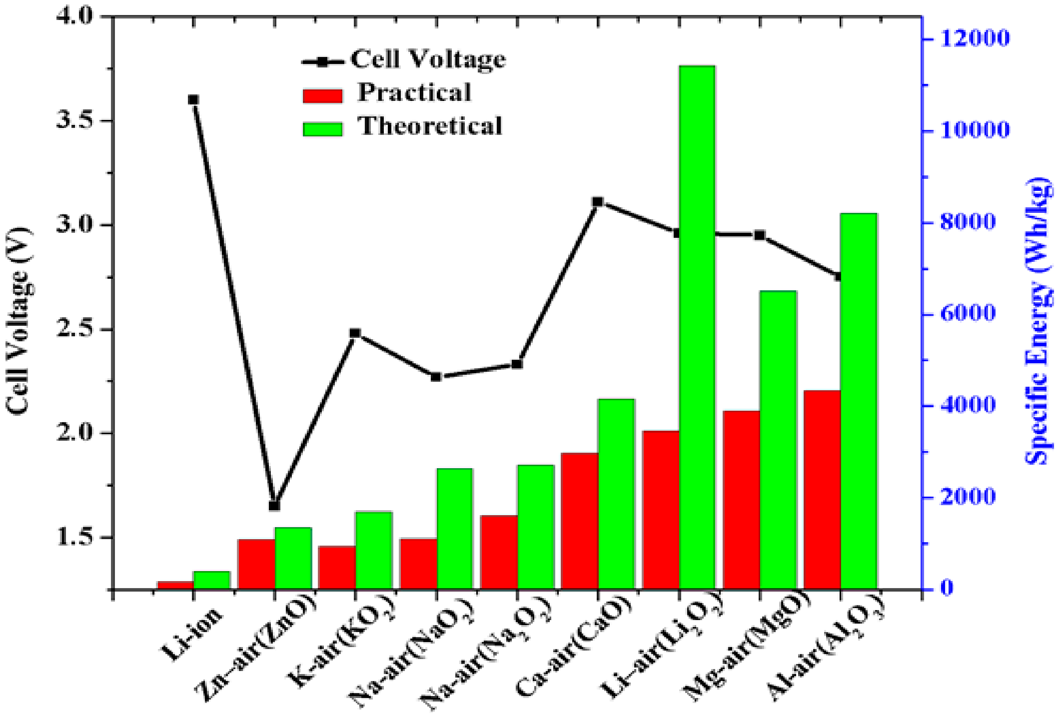

Figure 4. Theoretical and practical specific energy of commercial LIB and MABs with their corresponding theoretical cell voltages. The practical specific energy values are calculated based on the atomic weights of the discharge products, while the theoretical are calculated considering only atomic weights of the anode metal.

MABs, including Li-, Na-, Al-, Mg-, Fe-, and Zn-O_2 batteries, have garnered significant attention as potential replacements for LIBs, especially in the transportation sector [19]. Li-O_2 batteries (LOBs), with their exceptional specific capacity of ~3842 mAh/g, hold immense potential for revolutionary advancements in battery technology. These batteries are predicted to offer five to ten times' higher energy density than currently available rechargeable LIBs. Primarily designed for vehicle electrification, LOBs could potentially provide a driving range comparable to gasoline vehicles (~500 kilometers per charge). In 1996, Abraham et al. introduced the first secondary LOB using a non-aqueous solvent, where lithium peroxide is formed during discharge at the cathode [20]. While Li-O_2/Air batteries have demonstrated promising progress, significant improvements are still required before commercialization. These advanced battery technologies face several challenges that need to be addressed prior to widespread adoption. The practical application of rechargeable LOBs faces a notable obstacle known as "sudden death," attributed to the formation of an insulating layer on the cathode. In recent times, secondary SOBs have garnered significant attention, showcasing reported advantages over LOBs. With an impressive specific capacity of approximately 1500 mAh/g, which is more than double that of current Lithium-Ion Batteries (LIBs), SOBs emerge as a promising alternative to the prevailing LIBs. Rechargeable SOBs demonstrate low overpotentials even at high current densities (> 200 μA cm^{-2}) and achieve an energy efficiency of around 90% [21]. However, SOBs also experience "sudden death" during discharge and recharge cycles. The occurrence of sudden death is evident in a pronounced surge in cell potential towards the conclusion of the charge cycle, particularly at elevated current densities [21]. The fundamental cause of this abrupt failure during discharge is linked to restrictions in oxygen transport arising from the development of sizable NaO_2 crystals. Additionally, the buildup of these insulating NaO_2 crystals on the cathode surface hinders electrochemical reactions at the cathode-electrolyte interface [22].

MABs, including $Li-O_2$ and SOBs, face a multitude of challenges that hinder their widespread adoption. These challenges include complex parasitic side reactions, material instability across all battery components (anode, cathode, and electrolyte), poor conductivity, intricate interfacial phenomena, air impurities (particularly CO_2 and water vapor), and safety concerns. Furthermore, the currently achievable power and current densities are limited, posing a significant constraint.

2. Next generation Battery Technologies: Metal Air Batteries

MABs are a type of battery that utilizes a metal as the anode and oxygen from the air as the cathode. A catalyst is used to assist the reduction reaction of oxygen (ORR) at the cathode. The electrodes are connected by an electrolyte, which allows the flow of ions between them (Figure 5) [23]· Unlike other metal-ion batteries, such as LIBs, MABs do not require the storage of cathode reactants within the battery, as oxygen is readily available in the air. This unique feature enables the miniaturization of MABs, achieving the same energy capacity in a smaller volume or enhancing the energy density within the same volume [24].

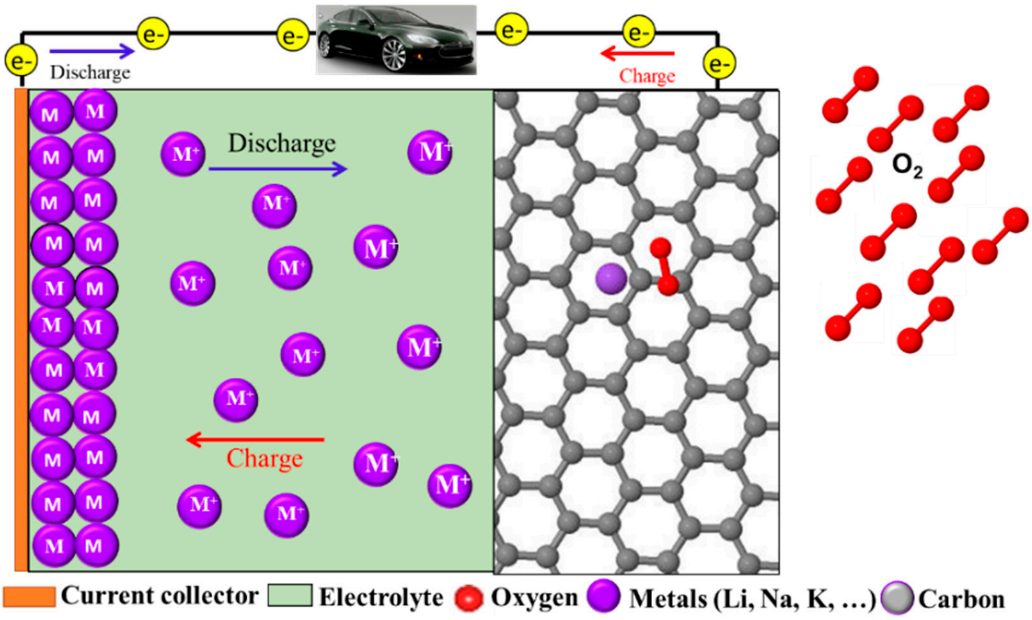

Figure 5. Schematic configuration of a Metal-air cell (Adopted from ref. 21).

MABs can be categorized based on the type of metal used, the electrolyte employed, and the underlying chemical reactions. In terms of the electrolyte, MABs can be classified as aqueous, aprotic solvent, or solid-state (or combinations of these) based on the electrolyte used. In terms of rechargeability, MABs can be categorized into three main groups: non-rechargeable or primary batteries, electrochemically rechargeable or secondary batteries, and mechanically rechargeable batteries. Primary batteries typically have their active materials replaced once they are depleted, a process known as mechanical recharging. Figure 6 illustrates a diagram of the most common MABs categorized based on the electrolyte used and their rechargeability.

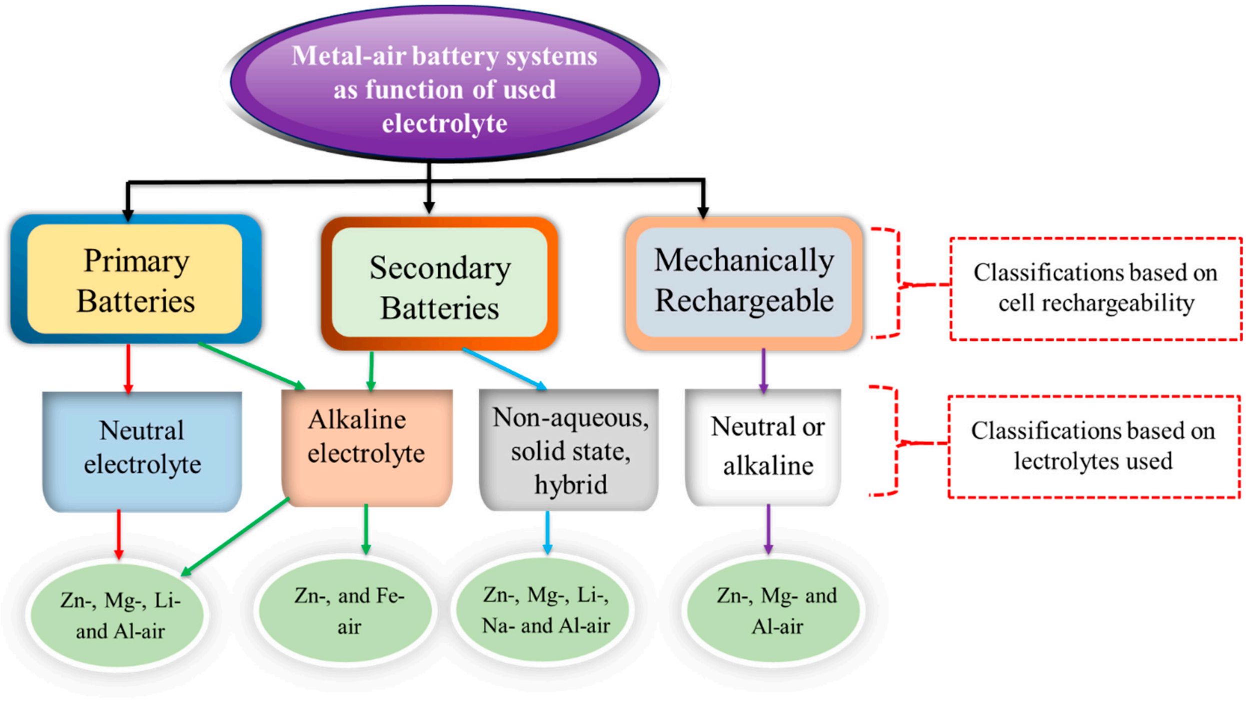

Figure 6. Classification of MABs based on electrolyte type and recharging mechanism [24].

Non-aqueous metal-oxygen batteries that are rechargeable rely on two crucial processes: the ORR and the OER. During discharge, the ORR takes place at the cathode, where dissolved oxygen molecules undergo reduction to form insoluble solid discharge products, typically oxides, peroxides, or superoxides. Simultaneously, at the anode, metal ions dissolve into the electrolyte. The OER, on the other hand, occurs during charging within the cathode. This process decomposes the discharge products, regenerating oxygen gas and dissolving metal ions back into the electrolyte. Concurrently, at the anode, metal ions are reduced to reform the metallic electrode and are deposited there. In essence, the ORR and OER work in tandem to enable the reversible storage and release of energy in non-aqueous metal-oxygen batteries.

2.1. Non-Aqueous Lithium-O_2 Batteries

Rechargeable LOB hold immense promise as the next generation battery technology, owing to their exceptional specific energy (~1700 Wh/kg) and the highest attainable specific capacity (~3842 mAh/g) [2,25]. Unlike state-of-the-art LIBs that depend on the intercalation of lithium ions in graphite, LOBs utilize lithium directly in its pure form as the anode, the lightest possible metal. Furthermore, the battery system breathes in oxygen gas from the ambient atmosphere, with oxygen gas (O_2) entering the cathode cell through purifying membrane technologies. While LOBs hold immense promise, several obstacles must be addressed before they can be commercially realized: (a) Contamination and Drying: Unsolicited atmospheric gases, such as N_2, CO_2, and water vapor in non-aqueous systems, can contaminate the cell, impairing its performance. Additionally, solvent evaporation can cause cell desiccation. (b) Gas Transport and Volume: The gas transport rate must be sufficiently high to sustain rapid discharging and charging. Moreover, the cell must provide adequate volume to accommodate the discharge products. (c) Discharge Product Morphology: The primary discharge product at the cathode is Li_2O_2, which can adopt various morphologies, such as disks, needles, films, and hollow spheres [26] (Figure 7b–f). Among these, biconcave disks, often referred to as "toroids," are the most common morphology (Figure 7b). While challenges remain, substantial strides have been made in the realization of MABs, particularly LOBs and SOBs. Further scientific and technical advancements are necessary to bring these promising technologies to market.

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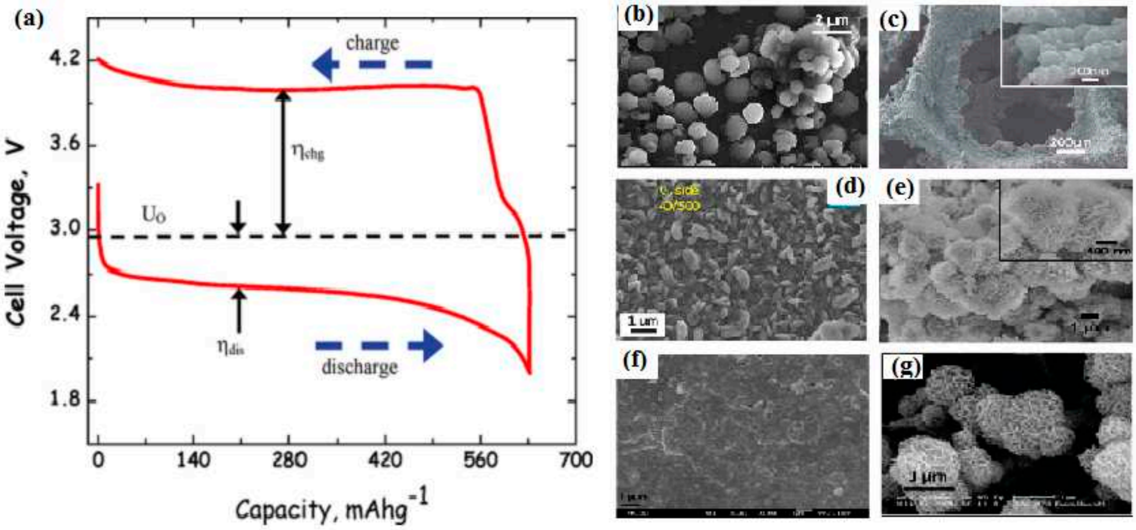
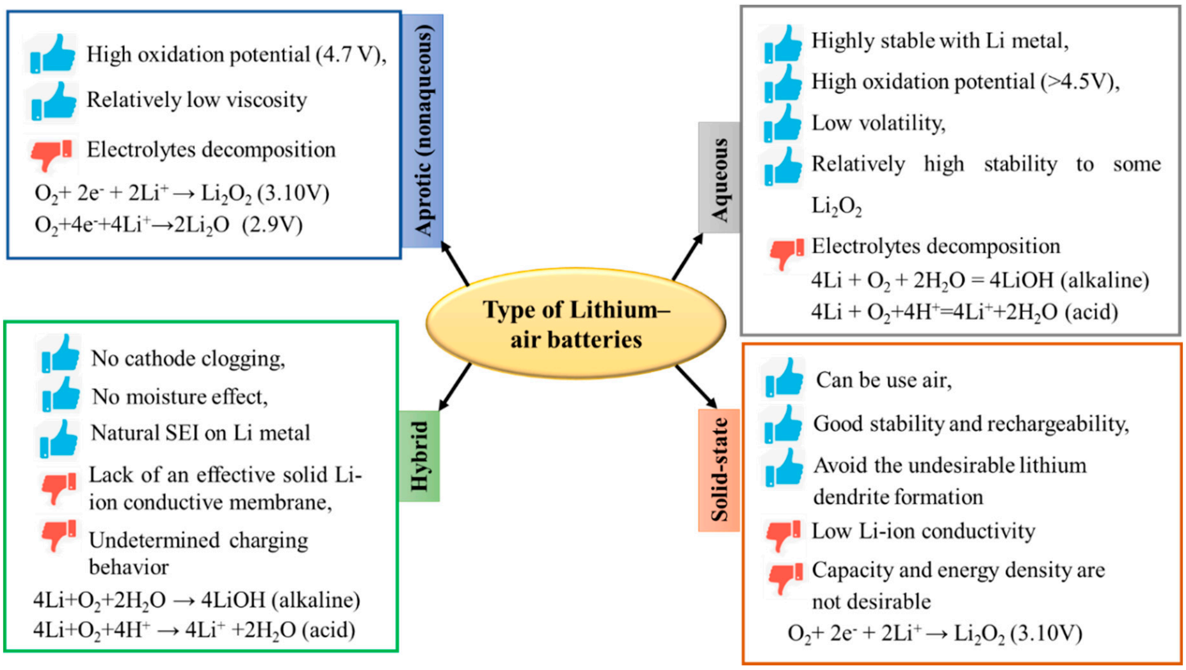


Figure 7. a) Galvanostatic discharge/charge cycle of a non-aqueous LOB [27] and SEM images of various lithium peroxide morphologies in the discharged cathode: b) Toroidal-shaped, c) spherical particles, d) elongated particles, e) close-packed nanosheets, f) rough thin films and g) porous ball-like [26].

Lithium-air batteries are divided into four distinct groups based on the electrolyte employed [28]: aprotic [20], aqueous [29], hybrid [30,31], and all solid-state [32] electrolytes (Figure 8). In all four types, lithium metal serves as the anode, while oxygen from the air acts as the cathode. The non-aqueous system shows particular promise due to its ability to reverse the lithium peroxide reduction product back to the initial ORR reagents, a process known as the OER. This reversibility establishes the rechargeability of the aprotic LOB. Since the aprotic Li-air battery has only demonstrated electrical recharge capability, significant research efforts have been focused on developing appropriate electrolyte solution systems [29].



👍 High oxidation potential (4.7 V),
👍 Relatively low viscosity
👎 Electrolytes decomposition
$O_2 + 2e^- + 2Li^+ \rightarrow Li_2O_2$ (3.10V)
$O_2 + 4e^- + 4Li^+ \rightarrow 2Li_2O$ (2.9V)

👍 Highly stable with Li metal,
👍 High oxidation potential (>4.5V),
👍 Low volatility,
👍 Relatively high stability to some Li_2O_2
👎 Electrolytes decomposition
$4Li + O_2 + 2H_2O = 4LiOH$ (alkaline)
$4Li + O_2 + 4H^+ = 4Li^+ + 2H_2O$ (acid)

👍 No cathode clogging,
👍 No moisture effect,
👍 Natural SEI on Li metal
👎 Lack of an effective solid Li-ion conductive membrane,
👎 Undetermined charging behavior
$4Li + O_2 + 2H_2O \rightarrow 4LiOH$ (alkaline)
$4Li + O_2 + 4H^+ \rightarrow 4Li^+ + 2H_2O$ (acid)

👍 Can be use air,
👍 Good stability and rechargeability,
👍 Avoid the undesirable lithium dendrite formation
👎 Low Li-ion conductivity
👎 Capacity and energy density are not desirable
$O_2 + 2e^- + 2Li^+ \rightarrow Li_2O_2$ (3.10V)

Figure 8. Types of lithium–air batteries.

In the discharge phase of aprotic lithium-air batteries, an oxidation reaction takes place at the anode. Here, lithium metal (Li) undergoes oxidation to yield lithium ions (Li^+) and electrons (e^-) (Li

$\rightarrow Li^+ + e^-$). Subsequently, these electrons traverse through an external circuit, while the lithium ions move towards the cathode. Upon reaching the cathode, they engage in a reaction with oxygen (O_2), resulting in the formation of lithium peroxide (Li_2O_2) or potentially lithium oxide (Li_2O) (refer to Figure 9). The reduction of oxygen at the cathode can take place through either a two-electron or four-electron process, as elucidated below [33]:

$O_2 + 2e^- + 2Li^+ \rightarrow Li_2O_2$ (3.10 V) (a)

$O_2 + 4e^- + 4Li^+ \rightarrow 2Li_2O$ (2.90V) (b)

These reactions are thought to be reversible under the application of external potentials, meaning that lithium metal can be deposited on the anode, and oxygen (O_2) can be released or produced at the cathode. The reaction potentials for both (a) and (b) are closely aligned, resulting in the predominant generation of both Li_2O_2 and Li_2O as the primary discharge products [15,20].

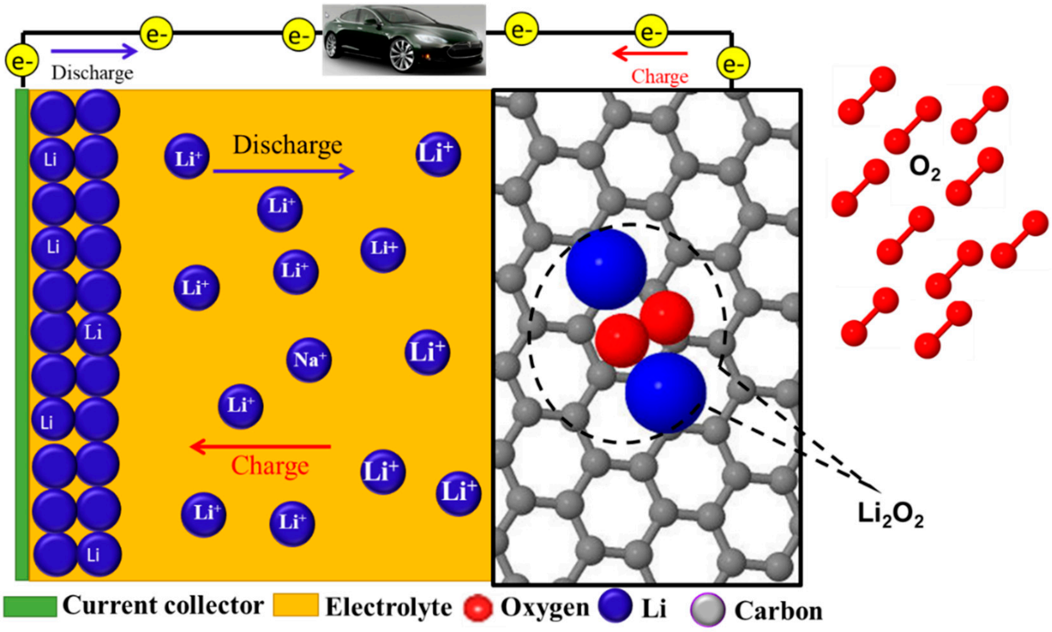


Figure 9. The schematic illustrations of a non-aqueous Li–air batteries and the oxygen electrode structure (Adopted from ref. 47).

2.2. Non-Aqueous Sodium–O_2 Batteries

LOBs have garnered substantial research interest owing to their remarkable theoretical energy density. Nevertheless, various inherent physical and chemical mechanisms occurring during battery operation impede the realization of their full potential [34]. These limitations stem from stability issues, including: (i) Lithium Dendrite Formation: Lithium metal anodes exhibit a tendency to form dendritic lithium deposits, which can pierce the separator and lead to cell short circuits.(ii) Contaminant Reactions: Lithium metal reacts with impurities present in the air (such as H_2O and CO_2) and certain electrolyte molecules, leading to performance degradation. (iii) Irreversible Oxygen Electrode Oxidation: The discharge product, Li_2O_2, undergoes further oxidation during charging at potentials exceeding 3.5 V, rendering it irreversible. (iv) Electrolyte Instability: The electrolyte degrades upon exposure to oxygen reduction products or intermediates.

Furthermore, Lithium-O_2 batteries suffer from low discharge/charge coulombic efficiency and limited cycle life. Replacing lithium with sodium metal has emerged as a promising strategy to address these limitations, particularly in terms of recyclability and overpotential reduction [35].

2.1.1. Electrochemical Reactions and Discharge Products

Similar to LOBs, SOBs consist of a sodium metal anode, an oxygen-permeable cathode electrode, and a non-aqueous electrolyte that facilitates the conduction of sodium ions. In the discharge phase, oxygen reacts with sodium ions in the presence of electrons, resulting in the formation of sodium oxides (NaO_2 or Na_2O_2), which are stored within the pores of the oxygen-permeable cathode. During the charging process, NaO_2/Na_2O_2 undergoes reversible oxidation to generate sodium ions and oxygen, while sodium ions are re-deposited as sodium metal on the anode. These fundamental principles are illustrated in Figure 10.

LOBs, where Li_2O_2 is widely acknowledged as the discharge product with lithium superoxide (LiO_2) as an intermediate, SOBs have exhibited various experimentally reported discharge products. These include sodium superoxide (NaO_2) [35–40], sodium peroxide (Na_2O_2) [41,42], sodium carbonate (Na_2CO_3) [43], sodium hydroxide (NaOH) [41], and hydrated sodium peroxide ($Na_2O_2{\cdot}2H_2O$) [44,45]. However, in sodium-air batteries, NaO_2 and Na_2O_2 emerge as the predominant discharge products. The overall reactions in sodium-air batteries can be summarized as follows:

$$\mathrm{Na^+ + e^- + O_2 \leftrightarrow NaO_2} \quad E^o = 2.27\ \mathrm{V\ vs\ Na/Na^+}, \quad \Delta G = -218.76\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{2Na^+ + 2e^- + O_2 \leftrightarrow Na_2O_2} \quad E^o = 2.33\ \mathrm{V\ vs\ Na/Na^+}, \quad \Delta G = -449.72.76\ \mathrm{kJ\ mol^{-1}}$$

Table 1 provides a comprehensive overview of the key properties that distinguish Na-O_2 and Li-O_2 systems. With a theoretical energy density of approximately 1108 Wh kg^{-1}, SOBs offer around 30% lower energy storage capacity compared to Li-O_2 cells [15]. However, SOBs exhibit a significant advantage in terms of charge overpotential. While typical LOBs operate at a charge overpotential of around 1300 mV, SOBs maintain a much lower overpotential of less than 100 mV [46]. The variance in discharge products is ascribed to the more pristine cell chemistry of SOBs when juxtaposed with Li-O_2 systems. Furthermore, SOBs exhibit enhanced coulombic efficiency, surpassing 95% during cycling, in contrast to LOBs [35].

Table 1. Theoretical parameter comparison for SOBs and LOBs across different discharge products [47].

	Na-O_2	Li-O_2
Cell chemistry	$Na^+ + O_2 + e^- \rightarrow NaO_2$ $2Na^+ + O_2 + 2e^- \rightarrow Na_2O_2$	$2Li^+ + O_2 + 2e^- \rightarrow Li_2O_2$
Cell voltage	E° (2 NaO_2) = 2.27 V (ΔG° = -437.5 kJ mol^{-1}) E° (Na_2O_2) = 2.33 V (ΔG° = -449.7 kJ mol^{-1})	E° (Li_2O_2) = 2.96 V (ΔG° = -570.8 kJ mol^{-1})
Overpotential (Discharge/ Charge)	$\eta_{dis} < 100$ mV $\eta_{ch} \approx 30$-100 mV	$\eta_{dis} \approx 300$ mV $\eta_{ch} \approx 1300$ mV
Energy density	1108 Wh kg^{-1} (NaO_2) 1605 Wh kg^{-1} (Na_2O_2)	3458 Wh kg^{-1} (Li_2O_2)
Theoretical capacity	1165 mAh g^{-1} (Na) 488 mAh g^{-1} (NaO_2) 689 mAh g^{-1} (Na_2O_2)	3861 mAh g^{-1} (Li) 1168 mAh g^{-1} (Li_2O_2)
OER/ORR efficiency	~ 78%	~ 93%

Earth Abundance of metal[1]	2.05%	0.0065%

[1] Earth’s crust composition in mass percent

Sodium's abundance in the Earth's crust, about 2.6% by weight, far surpassing that of lithium (4-55 orders of magnitude higher), holds the key to significantly lowering the cost of rechargeable sodium-air batteries compared to other battery technologies [48]. Moreover, sodium's inertness towards aluminum allows for the use of thin aluminum foil (lightweight and inexpensive) as the anode current collector, while copper or nickel is typically used in LOBs. Furthermore, the electrochemical similarities between Na-O_2 and Li-O_2 cells enable the extensive knowledge accrued over the past two decades in LOB research [49] to be cautiously applied to SOBs. This encompasses understanding electrolyte stability, efficient cathode support structures, and insights from observed degradation mechanisms in Li-O_2 cells, all of which can guide the initial design considerations for Na-O_2 systems. These collective advantages underscore the urgency of prioritizing the technological pursuit of developing a potentially sustainable and cost-effective SOB.

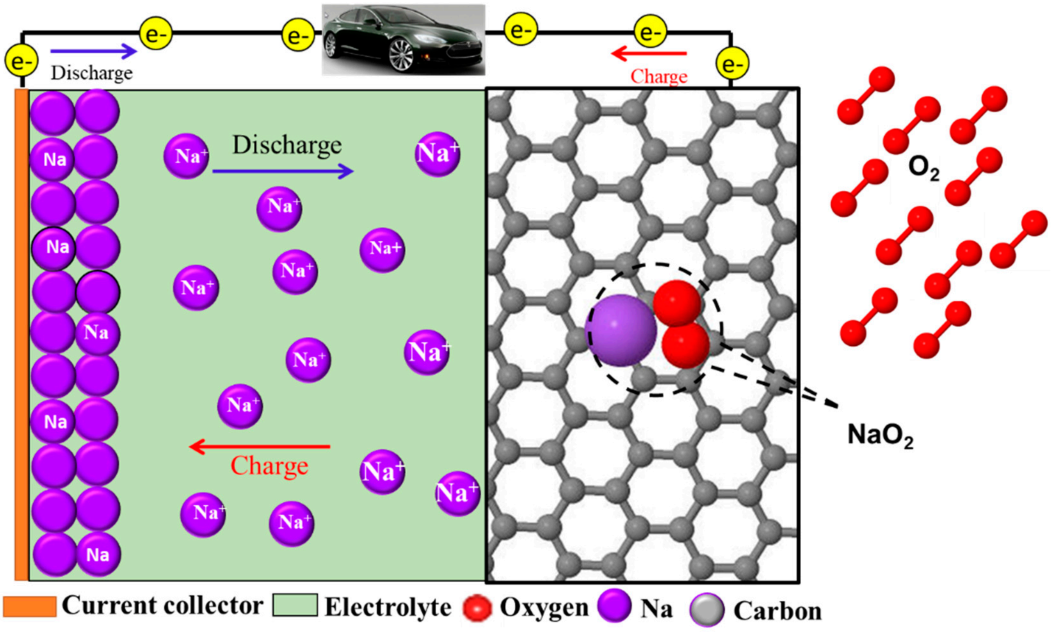


Figure 10. Schematic configuration of a Na–O_2 cell (Adopted from ref. 33 and 48).

Interest in SOBs surged following the first reported cell in 2011 by Peled et al. [50], which employed molten sodium metal as an anode. Overcoming challenges such as high cell impedance and dendrite formation, which were previously observed in LOBs, was achieved at 100 °C, leading to coulombic efficiencies of approximately 85%. In 2012, Janek et al. [35] successfully developed a SOBs that operates at room temperature, with face-centered cubic NaO_2 identified as the exclusive discharge product. However, subsequent studies have presented additional discharge products, and, conversely, some researchers have documented the formation of Na_2O_2 on the cathode following discharge. As illustrated in Figure 11, cells forming NaO_2 during discharge exhibit lower charging overpotentials (typically below 0.2 V) and demonstrate enhanced cell stability [35,37,46]. In contrast, cells forming Na_2O_2 during discharge exhibit significantly higher overpotentials (> 1.3 V) [41]. Additionally, cells forming Na_2O_2 have demonstrated poor rechargeability (< 10 cycles). Many of these drawbacks mirror those observed in the Li-O_2 system [37]. Despite these challenges, the selectivity of discharge products in SOBs remains a topic of debate, with two opposing views prevailing.

a) Thermodynamically Favored Na_2O_2: Na_2O_2 possesses a higher equilibrium potential (2.33 V) compared to NaO_2 (2.27 V), making it the thermodynamically favored discharge product (Figure 11).

This is supported by first-principles calculations conducted by Kang et al., leading to the conclusion that Na_2O_2 constitutes the more stable bulk phase of sodium in an oxygen environment. Nevertheless, their findings also indicate that NaO_2 demonstrates improved stability at the nanoscale [51]. Consistent with this observation, Liu et al. demonstrated the formation of Na_2O_2 film products during discharge when employing DME-based electrolytes in conjunction with graphene nanosheet cathodes [52].

b) Kinetically Favored NaO_2: The generation of NaO_2 involves a single electron transfer, while the formation of Na_2O_2 necessitates two electron transfers, indicating a kinetic preference for NaO_2 formation. DFT calculations carried out by Lee et al. indicate that NaO_2 is the most energetically favorable phase under standard conditions (300 K and 1 atm O_2) [53]. Kinetic investigations by Mekonnen et al. [38] further highlight that the discharge/charge overpotentials for Na_2O_2 growth/depletion are notably higher compared to those for NaO_2. Unraveling the conditions that favor NaO_2 as the discharge product is crucial, as it could pave the way for enhancing the electrochemical capabilities of SOBs.

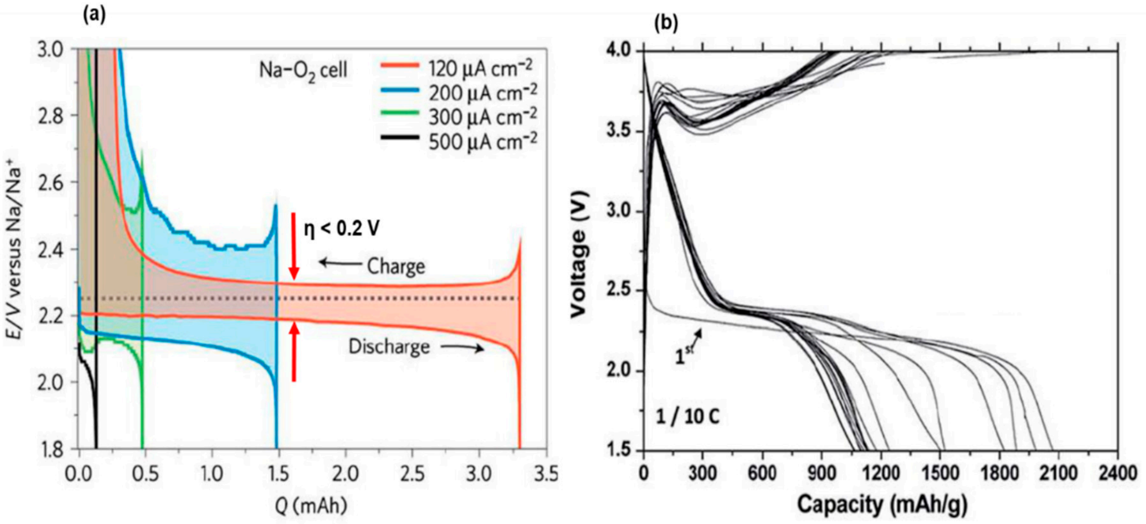


Figure 11. Typical charge–discharge curves of Na–O_2 cells: main discharge product a) NaO_2 [35] and b) Na_2O_2 [54].

2.2.2. Insight into the Reaction Mechanism in NASAB

During the discharge process of SOBs, cubic NaO_2 crystals that can reach micrometer dimensions are deposited. Two primary pathways for NaO_2 crystal growth in SOBs have been proposed and extensively researched [35]. These pathways are explained in detail below:

a)Solution-mediated pathway: Superoxide species dissolve in aprotic media and migrate towards the surface of pre-existing NaO_2 nuclei to facilitate further growth (Figure 12a) [35]. According to thermodynamic calculations by Shao-Horn and Lee, superoxide has significantly lower nucleation and dissolution energies compared to peroxide. Therefore, NaO_2 crystals could theoretically undergo growth through solution-mediated processes [53,55].

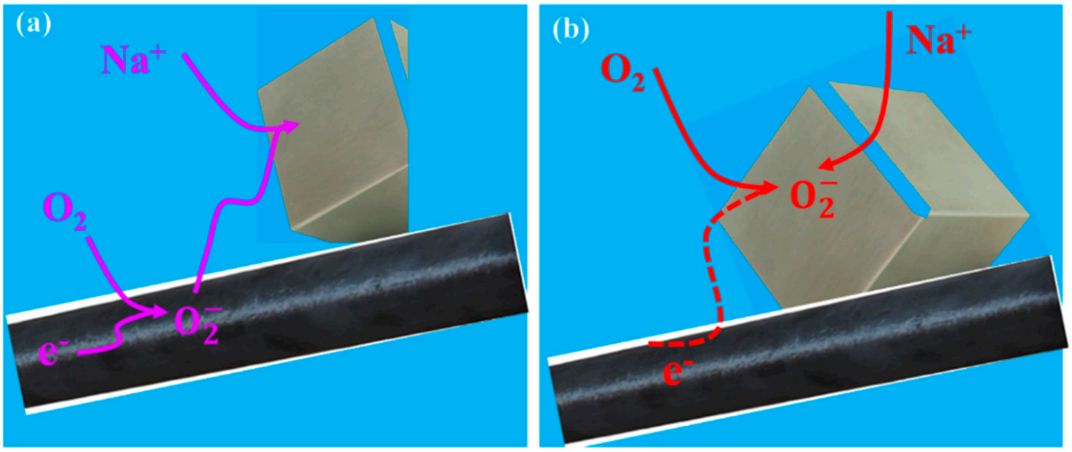


Figure 12. Schematic illustration of two potential growth mechanisms for NaO2 cubes during oxygen reduction to superoxide anions in the presence of sodium cations: a) Solution-mediated growth pathway and b) Surface-conductive growth pathway [35].

b)Surface-conductive pathway: Superoxide is created on the NaO_2 surface through direct reduction of oxygen (O_2) (Figure 12b). The superoxide then combines with Na^+ on pre-existing NaO_2 nuclei to support additional growth [35]. Lee et al. concluded, based on their computational analyses, that the electronic and ionic conductivities of superoxide exceed those of peroxide. Therefore, NaO_2 crystals could theoretically undergo expansion through surface-mediated processes [53,55].

Understanding the growth mechanism of SOBs holds significant interest as it has the potential to elucidate the alkali sodium-oxygen chemistry, a subject actively pursued by research groups globally.

3. Challenges in Non-Aqueous Metal-O_2/Air Batteries

3.1. Decomposition of the electrolyte

While non-aqueous Li-O_2 and SOBs offer the promise of higher energy densities compared to current LIBs, their long-term cycling performance remains a significant challenge. LOBs exhibit severe capacity fading, characterized by a decline in reversible capacity during cycling [56]. This capacity fade is attributed to the presence of highly reactive superoxide radicals, which can attack and decompose various electrolytes, particularly carbonate-based ones [57]. While glyme-based electrolytes have shown improved stability against superoxide attack compared to carbonate-based electrolytes, Bruce et al. illustrated through the use of Fourier Transform Infrared Spectroscopy (FTIR) and differential electrochemical mass spectrometry (DEMS) that glymes are vulnerable to superoxide attack [58]. Consequently, these electrolytes give rise to the creation of electrochemically inactive species, including lithium formate, lithium acetate, and lithium carbonate, on the porous carbon cathode. These insulating by-products act as passivating agents on the cathode surface, impeding oxygen reduction and contributing to the observed capacity degradation [59].

Despite exhibiting lower overpotential and superior chemical reversibility compared to LOBs, SOBs also suffer from premature cell death during cycling. Due to the similarities in their chemistries, it is hypothesized that analogous mechanisms of electrolyte decomposition by superoxide occur in both LOBs and SOBs [35]. Furthermore, carbonate-based electrolytes, such as propylene carbonates, have been shown to promote the deposition of Na_2CO_3 by-products [46]. Therefore, there is a notable requirement for research and development of electrolytes custom-designed for both LOBs and SOBs. However, designing an electrolyte that is simultaneously stable against decomposition on the cathode and anode sides remains a formidable challenge [60].

3.2. Degradation of the carbon cathode

The air cathode plays a pivotal role in MABs, as it is the site for both the ORR and OER. Consequently, the performance of the air cathode has a profound impact on the overall battery performance. However, several challenges hinder the development of effective air cathodes for both LOBs and SOBs. These challenges include:

1. Pore clogging: The precipitation of discharge products like Li_2O_2 during discharge can block the pores of the air cathode, impeding oxygen transport and limiting battery capacity.

2. Discharge products passivation layer: The formation of a passivating Li_2O_2 layer on the air cathode can hinder the ORR and OER processes, leading to reduced cell efficiency.

3. Electrolyte instability: Certain electrolytes can react with the air cathode, causing degradation and compromising battery performance.

4. Reaction and transport kinetics: The sluggish reaction kinetics and hindered oxygen transport within the air cathode can limit the overall discharge and charge rates [60].

In addition to these challenges, the instability of carbon cathodes in aprotic LOBs poses a further hurdle. Superoxide species can readily attack defects on the carbon surface during discharge, leading to the formation of Li_2CO3, which further degrades the cathode [59]. Similarly, NaO_2 can degrade carbon cathodes in Na-O_2 cells, restricting long-term cell performance [61]. To address these issues, the development of new cost-effective cathode materials with enhanced stability is crucial for the advancement of both Li-O_2 and SOBs.

3.3. Anodic Dendrite Growth

The uncontrolled growth of dendrites during charge-discharge cycles poses a significant challenge for secondary metal anodes, particularly for lithium and sodium. These protrusions can lead to internal short circuits within the battery, raising safety concerns and diminishing anode material utilization. Extensive research efforts have been dedicated to addressing this issue. While homogenous and highly conductive artificial protective layers have been developed, there remains a lack of materials that simultaneously offer adequate conductivity and safety. Additionally, new electrolytes and ion-conducting glass or glass-ceramic materials have been explored to mitigate dendrite formation. Furthermore, low charge-discharge efficiency is another challenge that needs to be addressed [60]. Consequently, lithium/sodium protection is a critical area of focus for enhancing the cycling life of Li/Na-O_2 cells.

3.4. Air Impurities

In the pursuit of advanced energy storage solutions, pure oxygen is typically used as the cathodic source in place of ambient air. This preference is due to the simplified kinetics associated with oxygen-based systems and the detrimental effects that various air components can have on these batteries. Transitioning from "metal-oxygen" to "metal-air" batteries presents significant challenges. While notable advancements have been made in aprotic Li-O_2 and SOBs in recent years, our understanding of air-based systems remains in its infancy [62].

Ambient air comprises approximately 78% nitrogen (N_2), 21% oxygen (O_2), 0.04% carbon dioxide (CO_2), and 0.4% water vapor (H_2O). N_2 can potentially react with lithium (Li) or sodium (Na) to form Li_3N or Na_3N, respectively, posing a concern when N_2 dissolves in the electrolyte and migrates to the metal anode. H_2O and CO_2 exhibit similar crossover effects and can react with superoxide or peroxide species at the cathode, forming carbonate and hydroxide species, respectively. Consequently, the cell chemistry in MABs deviates significantly from that of aprotic metal-oxygen batteries [63].

Among these airborne contaminants, CO_2 emerges as the most significant, owing to its high solubility in aprotic electrolytes and its elevated reactivity with Li_2O_2 (the primary discharge product in aprotic Li-O_2 cells) and NaO_2 or Na_2O_2 (the primary discharge products in aprotic Na-O_2 cells). These reactions result in the creation of insulating materials containing carbonate species, necessitating high overpotentials for decomposition. Therefore, comprehending the effects of H_2O and CO_2 is imperative for the advancement of Metal-Air Batteries (MABs) operating under ambient air conditions. This understanding is crucial for realizing practical applications of rechargeable Li/Na-air batteries.

4. Conclusions and outlooks

MABs exhibit a high energy density, rendering them appealing for applications such as electric vehicles and the storage of energy from renewable sources. Nevertheless, several constraints must be addressed before they can replace currently utilized LIBs. LIBs have approximately ten times lower theoretical energy density than MABs. The challenges associated with MABs encompass the development of a solid electrolyte interphase (SEI) layer and the occurrence of dendrite growth on the anode, the identification of an electrolyte that fulfills all the desired properties, and the stability of the cathode materials. Presently, researchers worldwide are engaging in intensive studies to gain a deeper understanding of these limitations and formulate effective solutions. Therefore, several critical aspects are imperative for the advancement and eventual commercialization of rechargeable MABs:

- Developing and synthesizing an innovative porous carbon material with enhanced conductivity, enabling the creation of an adequate and suitable three-phase interface that promotes effective charge/discharge processes
- Identifying bifunctional cathode catalysts with enhanced activity for both the ORR during discharge and the OER during charge to achieve a high round-trip efficiency.
- Designing stable electrolytes characterized by high oxygen (O2) solubility, enhanced ionic conductivity, low viscosity, and minimal vapor pressure.
- Creating a high metal ionic conducting separator and a high-throughput oxygen-breathing membrane utilized at the cathode to block H2O, CO2, and other air components except O2.
- Gaining a comprehensive understanding of the intricate chemical reaction mechanisms occurring during charge and discharge.

While numerous challenges must be addressed before commercially available MABs can be realized, their substantial advantages, particularly the high theoretical energy density, significantly surpass other conventional rechargeable battery systems. Intensive research, especially in the realm of materials, merits dedicated efforts towards unlocking the potential of this promising power source.

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