Metal air battery: A sustainable and low cost material for energy storage

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Abstract. Energy needs, depleting fossil fuel supplies and demanding sustainable energy alternatives is ever-increasing process. In the future energy network, power storage systems are one of the indispensable devices to buffer the irregular energy generation and renewable energy supplies. Therefore, it is important to design an innovative and efficient modern electrochemical storage system, combine with resource abundance, eco-efficient industrial methods, and life-cycle analysis. These issues are currently being addressed by few existing technologies but there are still theoretical and technical challenges in each case that needs to be talked again. Among these technologies Metal Air Battery (MAB) is a prominent solution and has recently been again into research these days. A metal air battery comprises a metallic anode in an appropriate electrolyte, and an embedded air cathode. The metals that can be used as anode may be first group metals such as sodium lithium, potassium etc. in second group other elements like magnesium, calcium etc. and third group aluminium and a few transition metals like Fe and Zn. Metal-air batteries are actually the combination of the design and working of traditional and fuel cell batteries. These have a high energy efficiency that is 5 to 30 times greater than lithium-ion batteries and are often considered a sustainable alternative. MABs considered are as eco-friendly, non-toxic, low cost and viable alternative as metals are abundant in nature. Metal-air batteries now a days are the most promising power storage systems with high power densities. A metal air battery comprises a metallic anode in an appropriate electrolyte, and an embedded air cathode. Metal-air batteries (MABs) combine the design features of traditional and fuel cell batteries. Some of the most common metal-air batteries include LAB (lithium air battery), SAB (sodium air battery), MABs (magnesium-air battery), AAB (aluminium air battery) and ZAB (zinc-air battery) etc.

Key Words: Metal Air Battery, Sustainable Energy Storage Device, Aluminum-air, Zinc-air

1. Introduction
Electrochemical energy storing systems are important components of future energy grid. Among the many, lithium ion battery and lead acid battery solutions are available, their performance is excellent and due to this these are extremely useful in our daily lives. Though LIBs are successful in their application areas, yet their energy and power densities may further be improved. The other successful energy storage system is lead acid battery LAB, but due to the toxicity of lead and absence of organized formal sector in its recycling makes it weaker again. As the demand of electrical vehicles is increasing day by day, the improvement in LIBs and LABs is need of the hour. In spite of various
benefits and advantages, LIBs have many problems. It is brittle and needs a shielded circuit to perform better. Shelf life is another apprehension, maximum lithium-ion batteries efficiency reduces just in its first year, whether the battery is in use or not. The efficiency cannot be increased more than 30%. Therefore, these are not much useful for transportation.

Metal air battery has also gained significant attention due to its higher energy capacity cost-effectiveness and environmentally friendly nature [1-2]. Metal air battery (figure 1) is a type of electrochemical cell where air is reduced and oxidation occur in metal. The anode may be made of metals and these metals may include alkali metals like lithium, potassium or sodium, alkaline earth metals like calcium and magnesium, some metalloid like Si, and Al or transition elements like iron and zinc. The electrolyte may vary from hydrous or non-hydrous depending on the type of the anode used. The other reduction electrode is made up of air, anode and cathode are separated by separators.

Figure 1. Schematic Representation of metal air battery

MABs have been invented in early of 19th Century, Maiche developed the first non-rechargeable Zn-air battery [3] and began selling its commercial products in 1932, since then ample amount of research and progress has been done in the area of MABs. After this research protic(aqueous) and non-protic (non-aqueous) batteries were invented. Batteries using aqueous electrolytes and anodic metals as iron, aluminum, and magnesium and air cathode were the early discoveries. Once the drawbacks of aqueous electrolytes were researched out, non-aqueous electrolytes combinations were invented. These batteries are inexpensive since the cathode source (natural oxygen) is abundant and the anode can be made from low cost metals [4]. MABs therefore seems to be one of the useful and advanced contenders for the upcoming requirements because of their higher heat capacity and power density as compared to other parallel batteries specially for EVs [5]. Metal air batteries are amongst the advanced class of primary and secondary cells. As the air is circulating throughout the cell in these batteries between the electrodes, they are at times classified as fuel cells. Since their invention in 1878, the metal air battery is an unappreciated innovation. The first recorded research in MAB was as aqueous Zn-air battery [6], which was designed in the most advanced ways and at par with today’s batteries
[7]. Hao Fan Wang and Qing XV (2019) explained a brief timeline (figure 2) from 1878-2018 and research progress of metal air batteries [8]. According to the timeline first Zn-air battery was proposed in 1878. The 21st century is still witnessing the promising progress in metal-air battery chemistry. In recent years, several metals, their combinations with oxygen and electrolytes, various catalysts are being researched for their increased usefulness, efficiency and economic values.
1.1. Types of metal air batteries

Commercial Li-ion batteries are doing well in electronics sector but comparing to metal air batteries their energy efficiency in terms of energy density is far less (approximately three to thirty times lower). (LABs) and (ZABs) i.e. Li and Zn metals as anodic metals have fascinated the world. LABs (with Li2O2 as the discharge product) can demonstrate a better theoretical value in terms of energy density and specific heat capacity (11,429 W-h/kg and 3,860 mAh/g respectively), and a cell voltage as high as 2.96 V. ZABs has the theoretical energy density of 1,350 Wh/kg which is approximately five times advanced than Li-ion batteries. The cost of both LABs and ZABs is far less as compare to lithium ion battery. If we see the other MABS, they also have their individual advantages. For instance, sodium-air batteries show lesser charge over potentials and aluminium-air batteries show the bulk volume capacity (8,040 Ah/L) [9]. Chunlion Wang described the progress in improving battery performance and advance manufacturing technologies for cathode, anode and electrolyte in MABs. Maximum research indicates that traditional alloys are preferred as electrode materials on anode as compare to alloys with nano-composites as these can reduce the other secondary reactions and enhance discharge capacity [10].

i) Zn-Air Battery- The zinc air batteries are the most appropriate for small-current applications such as hearing aids. They are the only one, successful and commercialized as primary cells in this category. Though, their shelf life and recharging capacity is limited, zinc-oxygen systems offer possibly the most immediate and reliable pathway to a viable secondary metal-air battery. The first battery that was invented in 1878 in the MABS category was the ZAB [8, 11]. A polymer electrolyte based ZAB and a novel dendrite resistant ZAB was designed by using multiphase electrolytes to conduct the Zn deposition and the OER [12]. Various theoretical and practical (electrochemical) properties of these batteries were explored using various instruments like EIS and galvanostatic discharge, SEM (scanning electron micrographs) and X-ray diffraction [13,14].

ii) Al-air Battery- The aluminium air battery (AAB) is highly suitable for electric vehicles (EVs) as an energy source. It is having an extraordinary energy density (theoretical value about 8100 Wh/kg), that is considerably better than LIBs. A new AAB is reported with an innovative organic non-aqueous electrolyte, this electrolyte consisted tetra-butyl-ammonium fluoride trihydrate salt dissolved in non-aqueous solvent like PC/TEG-DME, CAN etc. [15]. Another type of aluminium air battery with conventional 1-Ethyl-3-methylimidazolium chloride with AlCl3 electrolyte and Al foil and Pt/C as gas diffusion electrode [16,17].
iii) Na-air Battery- Sodium air battery is a new class of MAB with high specific heat energy of 1683 Watt hour/kg (theoretical value). Due to the abundance of sodium, low cost and eco-friendly nature, SAB is having applications in transportation [18]. SAB also comprising anode and cathode like any other metal air battery, and electrolyte with a separator in the battery case. A sodium air battery which comprised of carbon-fiber GDL and sodium triflate salt in diethylene glycol dimethyl ether as electrolyte was reported and its electrochemical properties were studied by EDS, XRD, SEM and Raman Spectroscopy etc. [19].

iv) Lithium air battery- The first secondary (that can be recharged) LAB was invented by K. Abraham. It was having Li as anode in the form of a membrane which was electrically conducting with carbon embedded air cathode [20]. Maximum Li-air batteries may possess highest energy density (about 3,458- Watt hour/kg- theoretical values) in all MABs range, that is quite advanced than that of Li-ion batteries is a promising contender for EES systems. Since its invention in 1996, wide research has been carried out to improve electrochemical reversibility of the oxygen electrode [21,22].

v) Vanadium Air Battery- A vanadium air battery is a modified vanadium redox flow battery (VRFB). The electrolyte is generally the (VO$^{2+}$/VO$_2^+$ couple) that is substituted by the oxygen on cathode. VAB may entirely be refuellable over semi-infinite cycles and good shelf life. A vanadium air battery/ redox flow battery that contains vanadium as anode and the air as reduction electrode and the electrolyte is MEA (coated with Ti Mesh) and VOSO$_4$ in H$_2$SO$_4$ electrolyte[23,24].

vi) Magnesium Air Battery- It is a combination of Mg as the anode and air is reduced at cathode. Reducing electrode is generally based on activated carbon. Sometimes catalysts are also used with a fine layer of aquaphobic polymer material and the metal sheet as the conductive element which is based on the electrode position of electrolyte material. Secondary Mg batteries are in the R&D stage and one of the important challenges has been to find the best suitable electrolytes combination. A biocompatible ionic liquid embedded Mg-air with a polymeric electrolyte material was demonstrated and to explain their electrochemical behavior, they used SEM, FTIR, EIS parameters [25]. The discharge behavior and characterization Mg air battery with tri-hexyl (tetradecyl) phosphonium chloride ionic liquid as an electrolyte and their characterization was explained in by FTIR, XPS and mass spectroscopy techniques [26].

vii) Potassium Air Battery-Potassium-oxygen batteries were invented in 2013 in Ohio State. These batteries could be more efficient than lithium-air batteries and also able to store twice the charge than present lithium-ion batteries. Another potassium air battery is designed with KPF6 dissolved in ether as an electrolyte. They used XRD and Raman spectroscopy for demonstrating its electrochemical behavior[27].

viii) Calcium Air Battery- Calcium is present in plenty amount in earth crust than Na and Mg. Calcium can be one of the best, nontoxic and one of the prominent metals in MABs range that with aqueous electrolyte can be proved to have many applications. Nirupama U Pujare in 1988 fabricated a calcium air battery with solid electrolyte of binary molten salt of CaCl$_2$ and Cao [28]. Calcium as metal for metal air batteries have potential to achieve a high electrical density at less manufacturing price [29].

x) Sn-air, Si air, Ge-air and Fe-air Batteries- The metals like Sn, Si, Ge and Fe are less used metals in MAB category. Byungkuk Ju in 2015 demonstrated a high temperature (75°C) solid electrolyte based tin air storage cell. By SEM and EDX element mapping study they explained that the Sn has the promising thermal oxidizing power near its melting point temperature [30]. Ein-Eli in 2010 described a MAB with silicon as anodic metal and air as cathode and ionic liquids as electrolytes. They used scanning electron microscopy, Energy-dispersive X-Ray spectroscopy and XPS studies to explain electrochemical behavior [31]. Joey et al. in 2013 fabricated a Ge based metal air battery with efficient PGE structure that was not shallow with precise interfacial structures. They were used a hierarchical nano porous anode and their electrochemical properties were described by SEM, XPS, X-Ray diffraction parameters [32]. In the battery design perspective, Fe has more than a few plus points: it is sturdy, it promises to provide enough energy per unit of mass. It is easily recycled and when use with alkaline electrolytes iron air batteries were having much potential for industrial investigations from 1970s to early 1980s [33]. The iron-air battery with alkaline electrolytes has a theoretical open circuit voltage of approx. 1.28 V and a specific heat energy of 764 Wh kg$^{-1}$(theoretical) [34].
1.2. Types of Electrolytes used in MABs
The electrolyte is a central component of metal air batteries. It is closely related to batteries efficiency. Each metal air system has its own unique specifications regarding electrolyte features [35]. Broadly following is the shortlisting criteria for electrolytes,

- Stable across different environment conditions.
- Low Volatility,
- Non toxic
- High in Oxygen solubility

Classically, we can categorize MABs into two categories according to their electrolytes. The first type is based on protic or aqueous electrolytes which are not affected by water or moisture and the other one is based on aprotic or non-aqueous which may be affected by atmospheric moisture or water. Metals that are highly reactive in aqueous electrolyte commonly used by non-aqueous aprotic electrolyte opposite to the aqueous MABs, non–aqueous MABs are still in their initial phase. Lithium, Sodium & Potassium can be taken as good such examples [21, 36].

1.2.1. Non aqueous electrolyte-based metal air batteries
i) Ionic liquid electrolyte: Electrolytes such as Ionic liquids are non-aqueous in nature. They contain two types of cations: a. large organic cations of organic / inorganic anions and b. organic solvent alkali metal ions, such as organic ethers, carbonates and esters.

Ein-Eli in 2010 developed a unique non-aqueous primary silicon air battery. a unique air battery with non-aqueous primary silicon as electrolyte [31]. This battery was conceived with following structure:

- Anode: Heavily doped n-type single crystal silicon wafers
- Electrolyte: 1-ethyl-3-methylimidazolium oligo fluoro hydrogenate [EMI (HF)2.3 F] ionic-liquid electrolyte at room temperature.
- Cathode: air oxygen

The resultant electrolyte show negligible corrosion rate and cell potential fluctuates between 1.1 to 0.8 with an average current densities ranging from 10-300 µA cm2 [31]. D. Gelman et.al.(2012) developed a unique non-aqueous Aluminum-air system, that contains (EMIm(HF)2.3) (1-ethyl-3-methylimidazolium oligo fluoro hydrogenate) which is non aqueous at room temperature, the resultant electrolyte based battery show 1.5mA/cm2 current density and producing capacity is above 140mAh/ cm2 and aluminium corrosion current is 25[µA/cm2]. The results from linear polarization experiment show high stability and negligible corrosion rates [37]. R. Ravel et.al. in 2014 employed EMI AlCl3 ionic liquid electrolyte for Al air battery at room temperature. This battery exhibits a low self-discharge rate and the capacity is 71mAh/cm [38]. M.A Deyab in 2017 used ionic liquid (1-Allyl-3-Methylimidazolium bis (trifluoro methyl sulfonyl) imide) (IL) in alkaline medium (4.0 N NaOH). The resultant electrolyte minimize the H2 gas evolution and corrosion rate and its capacity density increases to maximum value 2554mA/g [39].

ii) Solid electrolyte: Unlike aqueous electrolytes, solid-state electrolytes are different in dual characteristics of wettability and conductivity. Ryohei Mori (2019) created a secondary aluminium air system (i.e. rechargeable) with a solid electrolyte comprising AlCl3, urea, CMC and glycerin. The anode was made up of aluminium chloride and the air cathode was prepared by using a mixture of titanium nitride (TiN) and polyvinylidene difluoride (PVDF) in the ratio of 1: 0.3 molar, this mixture was flattened using a pelletizer at a pressure range of 4351 psi, and used as cathode. They claimed that in this battery the by-products like aluminum hydroxide and aluminium oxide were not formed as confirmed by various analysis like EDX, scanning electron microscopy and XPS, also it was shown that a stable electrochemical reaction was taking place due to presence of active surface layer [40]. Moran Balaish et.al. (2014) described the properties and characteristics of different solid electrolytes in lab, like alkyl carbonates, esters, nitriles, amides, sulphones and ionic liquids etc. [41]. Katsuro Hayashi et.al. (2013) fabricated a Na3Zr2Si2PO12 (NASICON a sodium superionic conductor) ceramic, solid electrolyte-based Na-air battery [42]. Atsushi Inoishi et.al. (2013) described a novel method for an oxygen transport type battery for Mg-air solid oxide batteries, this battery comprised of Ca- stabilized ZrO2 as an electrolyte [43].

iii) Polymer/composite/bio polymer electrolyte: Abraham and Jiang(1996) described non-aqueous and polymeric electrolyte based secondary (that can be recharged) Li air battery, which is constructed using the
PAN (polyacrylonitrile) based plasticized polymer electrolyte. During the discharge reaction Li ions are transported from the Li anode to the oxygen cathode, that can be stopped by using polyacrylonitrile based plasticized polymer as an electrolyte and a separator which will shield the cathode from anode and electrolyte medium. The polymeric electrolyte offers an appropriate solution to produce the power in lithium base system. This type of polymeric electrolyte-based batteries is especially suitable for powering small portable devices [20]. An alkaline glass-fiber-mat composite polymer electrolyte PEO-PVA that has excellent mechanical strength and electrochemical stability (1.2V) in solid state was used in Zn-air batteries described by Chun-Chen Yang and Sheng-Jen (2002) [11].

A biocompatible conducting polymer cathode and biocompatible polymer electrolyte was used for mg air batteries. It comprises a biocompatible para poly-pyrole (toluene sulfonic acid) cathode and a bioreabsorbable magnesium alloy anode. The biocompatible electrolyte used is made of choline nitrate (ionic liquid) embedded in a biopolymer, chitosan. This natural polymer electrolytes provide better mechanical stability to the battery and high ionic conductivity of 8.9 x 10-3 S cm-1. The assembled battery delivers a maximum volumetric power density of 3.9 W L-1. This battery has the application in biomedical monitoring devices like pacemakers for heart patients [44]. Zhao Zhang et al. (2014) used alkaline gel electrolyte based on polyacrylic acid (PAA) in all solid state Al-air batteries. [45]. Xiaoteng et.al. (2014) identified a Mg-air battery. It contains a biocompatible cathode of poly pyrrole-para (toluene sulfonic acid) and the biocompatible electrolyte using choline nitrate (ionic liquid), embedded in a biopolymer, chitosan. [44,45]. Hang et al. (2016) synthesized polymer composite gel electrolyte based on poly (vinylidene fluoride- hexafluoro propylene) (PVDF-HEP) polymer containing Al-doped Li0.33La0.56TiO3 particles protected by Silicon oxide (SiO2) film in Li-air battery [46]. Xiaoyue Fan et al. (2018) produced, with the addition of SiO2, a versatile and sandwich style Zn-air battery with a novel porous structured polyvinyl alcohol (PVA) based nano-composite polymer electrolyte (GPE). This strong, freestanding gel polymer electrolyte (PGEs) for Zn-air batteries and Al-air batteries shows good durability and high ionic conductivity [47]. Wang, et al. (2019) made a revolutionary paper al-air battery capable of inhibiting corrosion, simplifying the battery system and reducing storage of electrolytes. One big advantage of this is its low production cost [48]. Wending Pan et al. (2019) developed an economical, small and flexible cotton-based Al-air battery which has high performance, compactness and simple functioning [49]. Seongmin Ha et al. (2014) define the use of molten sodium and a polymer (ethylene oxide) based polymer electrolyte as the first non-aqueous rechargeable Na-air battery [50].

1.2.2. Aqueous Electrolyte Based Metal Air Batteries

A serious limitation of use of Li metal with aqueous electrolytes is it’s characteristic to react violently with water. As a solution, a layer of glass ceramic was placed above the Li electrode in 2004 [51]. This protected the metal electrode from reacting with water and at the same time allowing the required electro-chemical water. As a solution, a layer of glass ceramic was placed above the Li electrode in 2004 [51]. This protected the metal electrode from reacting with water and at the same time allowing the required electro-chemical water. As a solution, a layer of glass ceramic was placed above the Li electrode in 2004 [51]. This protected the metal electrode from reacting with water and at the same time allowing the required electro-chemical water.

i) Alkaline electrolyte: Da Pang Wang et al. (2015) designed Al-air batteries using compound of di-carboxylic acid such as C4H6O4 (SUA), C6H10O4 (ADA), C10H18O4 (SEA) as electrolyte additives in alkaline (NaOH) Ethylene glycol solution for AA5052 Al-air batteries. M. Xu et al. (2015) explained the improvement in Zn-air battery by the development in battery electrolytes vary from aqueous electrolytes to non-aqueous electrolyte which contain ionic liquid electrolyte, solid polymer and hybrid electrolytes. Arora et al. (2016) outlined the alkaline electrolyte problems and potential solutions for the Zn-air batteries. They suggest a baseline aqueous alkaline electrolyte saturated with ZnO composed of KOH, KF and K2CO3 [56].

ii) Hybrid electrolyte: M. Xu et al. (2015) explained the improvement in Zn-air battery using hybrid electrolytes varying from aqueous and non-aqueous electrolyte along with solid polymer electrolytes and Ionic liquid electrolytes [56].

iii) Room temperature ionic liquid (RTIL) for aqueous MABs the melted salts that maintains their liquid state at R.T. or below than that are known as RTIL. These have high thermal stability and do not catch fire easily. Therefore, received increasing attention as a substitute for alkaline electrolytes [57]. A positive effect of water addition on ionic interaction in RTIL electrolyte that was used in Zn-air batteries was explained [58,59]. Shuzhi Liu (2017) demonstrated a zinc-air system based on RTIL, which functions on a molten Li0.87Na0.63K0.50CO3 eutectic electrolyte [60].
iv) Quasi-Solid Flexible Electrolyte: Generally, quasi-solid versatile electrolyte made from alkaline aqueous electrolyte and polymers. Shichao Wu et al. (2016) suggested a feasible solution for the Lithium-air battery to prevent dendrites formation in the humid atmosphere by developing a superhydrophobic quasi-solid electrolyte (SHQSE) [61]. Joohyuk Park et al. (2015) developed a battery system with gelatin-based gel polymeric electrolyte in alkaline medium. This flexible ZAB cable type has proven successful operation with an external load [62].

| Metal Couples | EMF(V) | Theoretical Energy Density (Wh/Kg) | Voltage efficiency power(V) |
|---------------|--------|----------------------------------|-----------------------------|
| 2Li + O₂ → Li₂O | 2.90   | 11148                           | 3.16                        |
| 2Al + O₂ → Al₂O₃ | 2.71   | 8081                            | 2.93                        |
| 2Mg + O₂ → 2Mgo | 3.09   | 6813                            | 3.11                        |
| 2Fe + O₂ → Fe₂O₃ | 1.28   | 573                             | 1.35                        |
| Zn + 1/2O₂ → ZnO | 1.623  | 1331                            | 1.81                        |
| Cd + 1/2O₂ → CdO | 1.201  | 573                             | 1.349                       |

*Ref- [63]

2. Conclusion and future perspectives
After discussing and reviewing various aspects of MABs, we can conclude that metal air batteries demonstrate the great application as the energy storage system for different technologies. MABs are used as compact power sources for portable electronics and electric vehicles and are also used as persuasive energy transfer stations or energy storage systems for energy flow control among renewable energy generators. As the cost of air cathode is less and, in many cases, we can only use water or salt solution as an electrolyte that reduces the cost of metal air batteries much and we can run the vehicle on very less cost. The environmental sustainability of this battery is very good, less toxic metals can be used as anode and use of green electrolytes will increase its eco-friendly nature. To have a sustainable planet we need to reduce the carbon emissions. Use of hydrocarbon in petroleum products emits out substantial amount of carbon di oxide into our surroundings that is the reason behind the development of renewable energy sources, like hydropower, wind energy and solar power etc. According to Mckinsey more than 34 million EVs (hybrid, PHEVs and BEVs) are expected to be sold in 2030. Therefore, the requirement for energy storing devices arises, that can be a potential power storing system. Low-cost batteries with high power density, increased shelf life and ecofriendly nature are need of the hour. Many metal-air batteries could be found new applications in technologies such as electric vehicles, plug-in hybrid electric vehicles, robots, and electric power storing systems. The sustainable world is that, which produces less CO₂ emissions. If we consider that we are reaching to zero carbon emission mark by 2050, in that case the major part will be covered by EVs, and as per international energy agency at best 50 million EVs must be on the road by 2030.
3. References

[1] Lee J S, Tai Kim S, R. Cao, N S Choi, M Liu, Lee K T, Cho J 2011 metal air batteries with high energy density: Li Air versus Zn air Adv Energy Mater 1 34-50
[2] Wang Z L, Xu D, Xu J J, Zhang X B 2014 Oxygen electrocatalysts in metal air batteries from aqueous to nonaqueous electrolytes Chem. Soc. Rev 43 7746-7786
[3] Maiche L French Patent 1878 127 069
[4] Rahman M A, Wang X, Wen C 2013 High Energy Density Metal-Air Batteries: A Review J of the Electrochemical Society 160 A1759-A1771
[5] Bruce P G, Freunberger S A, Hardwick L J, Tarascon J M 2012 Li-O2 and Li-S batteries with High Energy Storage Nature Materials 11 19-29
[6] Vergnes M 1860 Improvement in the construction of voltaic gas-batteries US Patent 28317
[7] Yuan S, Ding F, Xiao J, Zhang J, Wu X, Sehiky P, Zhang J G, Wang Y, Liu J 2012 making Li-air batteries rechargeable material challenges Adv Funct Mater 23 987-1004
[8] Wang H F, Qiang X 2019 materials design for rechargeable metal air batteries Matter 1 565-595
[9] Yanguang L, Jun L 2017 Metal air batteries: will they be the future electrochemical energy storage device of choice? ACS Energy Lett. 2 1370-1377
[10] Wang C, Yangchao Y, Jiajia D, Xiangliang J, Joshi P, Zhang Y, Anning Hu 2019 recent progress of metal air batteries a mini review Appl. Sci 9 2787
[11] Yang C C, Sheng J L 2002 Alkaline composite PEO-PVA glass fiber mat polymers electrolyte for Zn-air Battery J. Power Sources 112 497-503
[12] Huang S, Hui L, Pucheng W, Wang K, Xiao Y, Zhang C C 2020 A dendrite-resistant zinc-air battery J. Sci. 23 6 101169.
[13] Fu J, Cano Z P, Park, M G, Yu A, Fowler M, Chen Z 2017 electrically rechargeable zinc-air batteries: progress, challenges, and perspectives Adv. Mater 29 604685
[14] Li Y, Gong M, Liang Y, Feng J, Kim J E, Wang H, Hong G, Zhang Z, Dai H 2013 Advanced Zinc-Air Batteries Based on High Performance Hybrid Electro catalysts. Nat. Commun. 4 1805
[15] Natasha R L, Shira L, Yohanan E, Eli Y E 2020 Hybrid Ionic Liquid Propylene Carbonate based Electrolytes for Aluminum-air Batteries ACS Applied Energy Materials 3, 3, 2585-2592
[16] Bogolowski N, Drillet J F 2017 an electrically rechargeable Al air battery with aprotic liquid electrolyte ECS Transactions 75 22 85-92.
[17] Yisi L, Qian S, Wenzhang K, Keegan R, Adair, Jie L, Xueliang S 2017 A comprehensive review on recent progress in aluminum–air batteries Green Energy & Environment 2 3 246-277
[18] Xiaolong X, Kwan S H, Duc A D, Kwun N H, Wang H 2019 recent advances in hybrid sodium–air batteries. Mater. Horiz. 6 1306-1335
[19] Hartmann P, Conrad L, Bender, Vrascar M, Katharina D A, Garsuch A, Janeck U, Adelhelm P 2012 A rechargeable room-temperature sodium superoxide NaO2 battery Nature Materials 12(3) 228-232
[20] Abrahm K M, Jiang Z 1996 A polymer electrolyte -based rechargeable lithium- oxygen battery. Electrochem Soc.143 1.
[21] Grande L, Paillard E, Hassoun J, Park J B, Lee Y J, Sun Y K, Passerini S, Serosati B 2015 The Lithium/Air Battery: Still an Emerging System or a Practical Reality? Adv. Mater 27 784- 800
[22] Li Y, Wang XG, Dong S M, Chen X, Cui G L 2016 Recent advances in non -aqueous electrolyte for rechargeable Li- O2 batteries Adv. Energy Mater 6 1600751
[23] Hossiney S S, Saakes M, Wessling M 2011 A polyelectrolyte membrane-based vanadium/air redox flow battery Electrochemistry Communications 13 751-754
[24] Rahaman F, Skyllas K, Maria 2009 Vanadium redox battery: Positive half-cell electrolyte studies Journal of Power Sources 189 1212-1219
[25] Zhang T, Zhanliang T, Chen J 2014 Mater. Horiz. 1 196-206
[26] Timothy K, Somers A, Angel A J, Torrierio D R, Farlane M, Patrick H, Maria F 2013 Discharge behavior and interfacial properties of a magnesium battery incorporating triethyl (tetraethyl) phosphonium based ionic liquid electrolytes, Electrochimica Acta 87 701-708
[27] Xiaodi R, Yiyung W 2013 A Low-Over potential Potassium Oxygen Battery Based on Potassium Superoxide J. Am. Chem. Soc. 135 2923--2926
[28] Nirupama P U, Krystyna WS, Sammells A F1988 A Calcium Oxygen Secondary Battery Journal of ECS 135 1
[29] Reinsberg P, Christoph J, Bondue, Baltruschat H 2016 Calcium Oxygen Batteries as a Promising Alternative to Sodium Oxygen Batteries J. Phys. Chem. 120 39 22179--22185
[30] Hyungkuk J, Lee J 2015 High temperature liquid Sn-air energy storage cell J energy chem.24 5 614-619
[31] Cohn G, Eli Y E 2010 Study and development of non-aqueous silicon-air battery J. Power Sources 195 4963–4970
[32] Ocon J D, Kim WJ, Sunghyun U, Bangjin S M, Lee J 2013 An etched nano porous Ge anode in a novel metal-air energy conversion cell Phys. Chem. Chem. Phys. 15 6333-6338
[33] Vijayamohan K, Balasubramanian T S , Shukla A K, 1991 J. Power Sources 34 3 269-285
[34] Ojefors L, Carlsson L 1978 J. Power Sources 2 Issue 3 287-296
[35] Manthiram A, Yu X, Wang S 2017 Lithium battery chemistries enabled by solid-state electrolytes Nat Rev Mater 2 16103
[36] Lu J, Li L, Park JB, Sun YK, Wu F, Amine K 2014 Aprotic and Aqueous Li–O2 Batteries. Chem. Rev.114 5611–5640
[37] Gelman D, Shvartsev B, Eli Y E 2014 Aluminum-Air Battery Based on an Ionic Liquid Electrolyte J. Mater. Chem. A 2 20237-20242
[38] Revel, Renaud, Audichon, Thomas, Gonzalez, Serge 2014 Non-aqueous aluminum-air battery based on ionic liquid electrolyte Journal of Power Sources 272
[39] Deyab M 2017 1-Allyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide as an effective organic additive in aluminum-air battery Electrochimica Acta 244
[40] Ryoei M 2019 A novel aluminum-air secondary battery with long-term stability RSC Adv. 4 1982
[41] Balalish M, Alexander K, Eli Y E 2014 A critical review on lithium–air battery electrolytes Phys.Chem.Phys.16 2801
[42] Hayashi K, Shima K, Sugiyama F 2013 A Mixed Aqueous/Aprotic Sodium/Air Cell Using a NASICON Ceramic Separator Journal of The Electrochemical Society 160 9 A1467-A1472
[43] Inoishi A, Wan JY, Shintaro I, Ishihara T 2013 Mg air oxygen shuttle batteries using a ZrO2-based oxide ion-conducting electrolyte Chem. Commun. 49 4691-4693
[44] Xiaotong J, Yang Y, Wang C, Zhao C, Vijayaraghavan R 2014 Biocompatible Ionic liquid – Biopolymer electrolyte enable thin and compact mg air batteries ACS Applied materials and Interfaces 6 23 21110-21117
[45] Zhang Z, ChunCheng Z, Liu Z, Yu Y, Zuo Y, Song Y 2014 All-solid-state Al air batteries with polymer alkaline gel electrolyte J. Power Sources 251 470-475
[46] Hang T.T.Le, Duc T N, Ramchandra SK, Guozhang C, Choong N P, Dhan J 2016 composite gel polymer Electrolyte based on Poly(vinylidene fluoride- hexafluoropropylene) (PVDF-HFP) with Modified Aluminum Doped Lithium Lanthanum Titanate (A-LLTO) for high performance Lithium Rechargeable Batteries ACS Appl Mater Interfaces 8 20710-20719
[47] Xiayue F, Liu J, Zhisuang S, Xiaopeng H, Yida D, Zhang C, Hu W 2018 Porous nano composite Gel polymer electrolyte with High Ionic conductivity and superior electrolyte retention capability for long-cycle-life Flexible Zinc-air Batteries Nano Energy 11 957
[48] Wang Y F, Kwok H, Wending P, Zhang H, Leung D 2019 Innovative paper based AI air batteries as a low cost and green energy technology for the mini watt market J. Power Sources 414 278-282
[49] Wending P, Wang Y, Holly Y H, Kwock D, Leung Y C 2019 A Low-Cost Portable Cotton-Based Aluminum- Air Battery with high specific energy, Energy Procedia 158 179-185
[50] Seongmim H, Kim J K, Aram Choi, Youngsik Kim, and Kyy Tae Lee Seongmin Ha, Jae-Kwang Kim, Aram Choi, Youngsik Kim,and Kyy Tae Lee 2014 Sodium Metal Halide and Sodium Air Batteries Chem Phys Chem 15 10 1971-1972
[51] Mein J T, Peilin B L, Xiaoming G, Zhaolin L, Zong Y, Xian J L 2018 Acrylamide derived freestanding polymer gel electrolyte for flexible metal air batteries J. Power Sources 400 566-571
[52] Visco SJ, Katz BD, Nimon YS, Jonghe D LC 2007 protected active metal electrode and battery cell structures with non-aqueous interlayer architecture U.S. Patent 7282295 B2
[53] Visco SJ, Nimon YS 2010 Active Metal aqueous Electrochemical Cells and Systems U.S. Patent 7645543 B2
[54] Clark S, Latz A, Horstmann B2018 A Review of Model-Based Design Tools for Metal-Air Batteries Batteries. 4(1).5
[55] Wang D P, Zhang D Q, Lee Y K, Gao L X 2015 Performance of AA5052 alloy anode in alkaline ethylene glycol electrolyte with dicarboxylic acids additives for aluminum-air batteries J. Power Sources 297 464-471
[56] Xu M, Ivey D G, Xie Z, Qu W 2015 Rechargeable Zn-air batteries: Progress in electrolyte development and cell configuration advancement J. Power Sources 283 358-371
[57] Arora R, Mainar, Leonet O, Bengoechea M, Boyano I, Meatza I D, Kvasa P, Merfl A, Blazquez A 2016 Alkaline aqueous electrolytes for secondary Zinc-air batteries: an overview Int J.Energy Res 40 1032-1049
[58] Chen P, Zhang K, Tang D, Liu W, Meng F, Huang Q, Liu J 2020 Recent Progress in Electrolytes for Zn air batteries 8 372
[59] Ghazvini M S, Pullerikuthi G, Cui T, Kuhl C, Endres F 2018 Electrodeposition of zinc from 1-ethyl-3- methylimidazolium acetate-water mixtures: investigations on the applicability of the electrolyte for Zn-air batteries J. Electrochem. Soc. 165 (9) D354-363
[60] Liu S, Wei H, Baochen C, Liu, Xianjun, Zhao F, Stuart, Jessica, Licht 2017 A novel rechargeable zinc-air battery with molten salt electrolyte J. Power Sources 342 435-441

[61] Shichao W, Jin Y, Kai Z, Songyan B, Liu Y, Qiao Y, Ishida M, Zhou H 2016 A Super hydrophobic Quasi-Solid Electrolyte for Li O2 Battery with Improved Safety and Cycle Life in Humid Atmosphere Adv. Energy Mater 7 4 1601759

[62] Park J, Park M, Nam G, Lee J S, Cho J 2015 All-Solid-State Cable-Type Flexible Zinc air Battery Adv. Mater 27 (8) 1396-1401

[63] Blurton K F, Sammells A F 1979 Metal Air Batteries: Their status and potential-A Review J. Power Sources 4 263-279