Chapter 1

Introduction

“A battery is a promise of power waiting to be unleashed.”

-J. B. Goodenough

1. Introduction

1.1 Current status of the global energy infrastructure

The continuous rise of greenhouse gases in the atmosphere escalates the threat of climate change with severe impact on the people, global economy and nature [1,2]. The United Nations has laid down several concerted efforts and consultations to mitigate the growing energy crisis. It primarily focuses on the control of carbon footprints in the environment by significantly reducing the use of fossil fuel [3-6]. Several discussions (e.g. COP21 as a result of which Paris agreement was formed) had resulted in consensus on carbon neutral economy and on a shift from fossil fuel-based energy to more sustainable renewable energy [4,5]. Moreover, our world is also facing energy related crisis due to various on-going global geopolitical events [7-9]. These events severely disrupt the energy supply chains which is causing continuous rise in the crude oil prices. As one of the prime drivers of the world economy, high energy cost severely affects the livelihoods of millions of people [9]. Moreover, the world economy is now far more interconnected than it was 50 years ago, amplifying the crisis's impact. This interconnection makes this energy crisis a truly global one. The post-pandemic era has seen even an increased impact of energy shortages [10]. Hence, the world community is inclined to renewable energy sources. According to statistics, the current energy production is 14 TW which, must be doubled by 2050 to meet the goal of zero-carbon emission economy [11-14]. The primary obstacle on the way to success is that it must be accomplished without sacrificing the objective of zero carbon emissions. That is why the global imperative now is to provide platform for sustainable energy development complemented by advanced energy storage technologies.

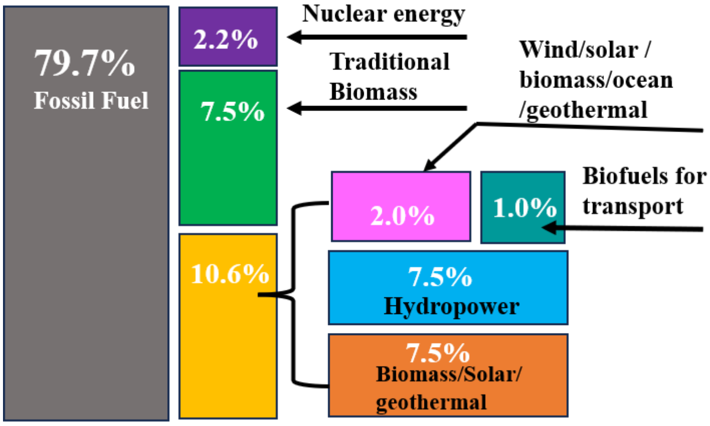

Figure 1.1 Schematic of current global energy usage [reproduced from data in ref 10-15].

1.2 Integration of renewable energy into the grid

Renewable energy can be of different forms such as wind, solar, tidal, biomass, geothermal etc. These resources are contributing hugely in the sustainable global development initiatives and to reduce dependence on fossil fuel-based energy resource [15-17]. There is continuous rise in the production of energy from renewable sources. But the main challenge associated with these sources are their intermittent, variable and dispersed nature. A rapid fluctuation in the energy generation can be witnessed with these resources which could result in the inability to deliver energy in a continuous manner [16]. The need for energy storage systems is paramount here to sustain the on-demand utilization of the energy [17]. In the current scenario, the electricity supply based on the centralized grid-based electricity delivery system is becoming the backbone of these supply chain although the access to these facilities is limited to certain geographical locations [18,19]. The unpredictability in the regional, seasonal, and weather patterns makes it even more challenging to precisely assess or even define resource adequacy. Studies predict that the current grid infrastructure can sustain only a minimal percentage of energy produced worldwide which is certainly inadequate to cope up with the global need [20-22]. Also, the immobility of these energy resources and the rapidly changing load patterns add extra pressure in the existing world grid infrastructure. Nonetheless, decentralized off-grid supplies are becoming feasible choice for areas without access to the grid. Grid facility with secured storage capacity could possibly mitigate these pressing global challenges of storing the enormous energy produced from these renewable resources [23]. Therefore, integration of energy storage devices into the current grid infrastructure is becoming indispensable in order to assist and stabilize the grid. With this integration, grid operators may better control supply and demand variations, reduce grid instability, and improve dependability [24,25]. The large-scale battery storage systems also help to create a more resilient energy network by supporting the shift to decentralized energy systems like microgrids and offering backup power during blackouts.

1.3 Energy storage – A global solution to restore grid infrastructure

The primary incentive of energy storage deals with the transformation of one form of energy into another type at an efficient and reliable manner. By storing excess energy during times of low demand and releasing it during peak consumption, energy storage systems ensure a steady and reliable power supply. In addition to stabilizing the grid and facilitating the integration of renewable energy, energy storage also plays a key role in providing backup power during outages and reducing overall energy costs [26]. Despite its importance, challenges remain which include the high cost of certain storage systems and the need for efficient, large-scale solutions [27]. In terms of large-scale production, the storage systems available can be classified into four main categories: mechanical, chemical, electrical and electrochemical. These energy storage systems include technologies like flywheels, pumped-storage hydroelectricity (or pumped hydro, PHSs), and compressed air energy storage (CAES). The rechargeable or secondary battery technologies belong to the electrochemical energy storage system [28-31]. In the current scenario, among all the storage technologies around the world, the pumped hydroelectric systems (PHSs) are mostly utilized to store the output power storage capacity [30,31]. Studies reveal that 99% of the 127000 MW of discharged power output worldwide is procured from these PHSs [22,33]. Although PHSs are the most matured technology available for now, electrochemical energy storage (EES) technologies are also drawing lots of interest due to some desirable aspects including low maintenance, extended cycle life, adjustable power and energy characteristics, high round-trip efficiency, and pollution-free operation [34].

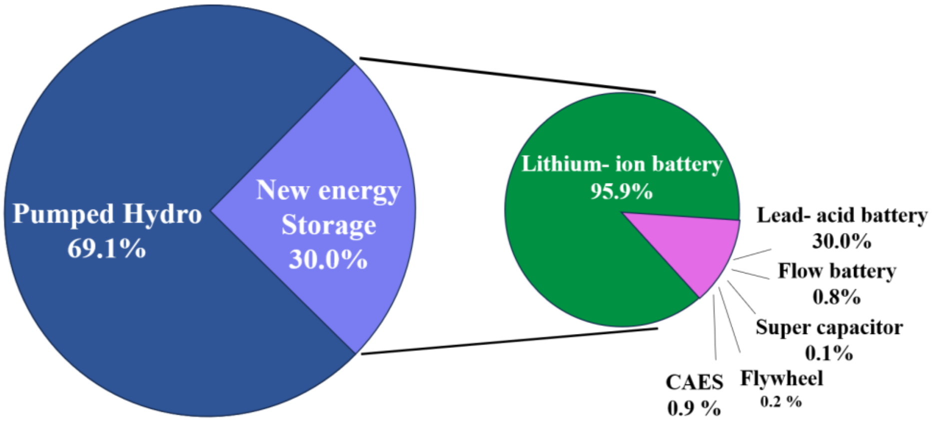

Figure 1.2 Schematic of current global energy infrastructure [reproduced from the data in ref. 28-33].

1.4 Electrochemical energy storage systems

Electrochemical energy storage systems such as batteries and supercapacitors rely on the process of storing electrochemical energy through reversible electrochemical reactions. These systems store and release energy by facilitating ion movement between two electrodes through an electrolyte during subsequent charging and discharging cycles [35-37]. Basically, the electrochemical reaction that occurs at the electrodes defies the performance characteristics of the storage device, which is measured in terms of capacity, voltage, and cycle life. Electrochemical storage systems are widely used across various applications, from portable electronics to electric vehicles and grid-scale energy storage, due to their ability to store and release large amounts of energy efficiently. There exist various electrochemical energy-storage technologies, including batteries, redox flow batteries, electrochemical supercapacitors, and fuel cells which are differed in their energy storage methods [38,39]. Batteries store energy via electron transfer reactions, changing the oxidation states of reactants as electrons move between the anode and cathode. Redox flow batteries operate similarly, but the redox-active species circulate in liquid electrolytes, allowing for scalable energy storage. Supercapacitors store energy through capacitive charging, where energy accumulates at the interface between the electrode and electrolyte, offering rapid charge/discharge cycles but lower energy density. Fuel cells generate electricity through a continuous chemical reaction between external reactants (such as hydrogen and oxygen) without storing energy, producing electricity, water, and heat as byproducts. While batteries, redox flow batteries, and supercapacitors function as closed systems, fuel cells rely on a constant supply of fuel to operate [40-43].

1.5 Batteries

Batteries are devices that store chemical energy and convert it into electrical energy through electrochemical reactions. At the core of a battery are two electrodes: the anode (negative terminal) and the cathode (positive terminal), which are separated by an electrolyte that facilitates the movement of charged particles (ions) between them. When a battery is in use, electrons flow from the anode to the cathode through an external circuit, providing electrical power. The electrolyte helps to maintain the balance of charge by allowing ions to move between the two electrodes [44,45]. Different types of batteries use various chemical reactions and materials; for instance, lithium-ion batteries, commonly used in smartphones and electric vehicles, use lithium containing salts as their electrolyte and materials which can host Li^+ ions as electrodes. Other batteries, like lead-acid ones found in cars, rely on lead and sulfuric acid [46,47]. Battery capacity, often measured in milliampere-hours (mAh) or ampere-hours (Ah), determines how much energy a battery can store and how long it can power a device. The most widely utilized electrochemical devices in the present-day scenario are lead-acid, lithium-ion, nickel–cadmium, and other flow batteries [48,49]. Among all these, lithium-ion batteries (LIBs) are considered to be the most advanced and well-developed electrochemical energy storage technology. At present, considering the extraordinary benefits of LIBs like high energy and power density, long cyclability with low self-discharge, they are employed extensively in various sectors. Over the past decades the transport and the portable device sector have seen revolutionary growth due to the fast advent of LIBs into the market. The global EV market has seen an upward push in last five years by virtue of the tremendous incorporation of LIBs into these set ups [50-52].

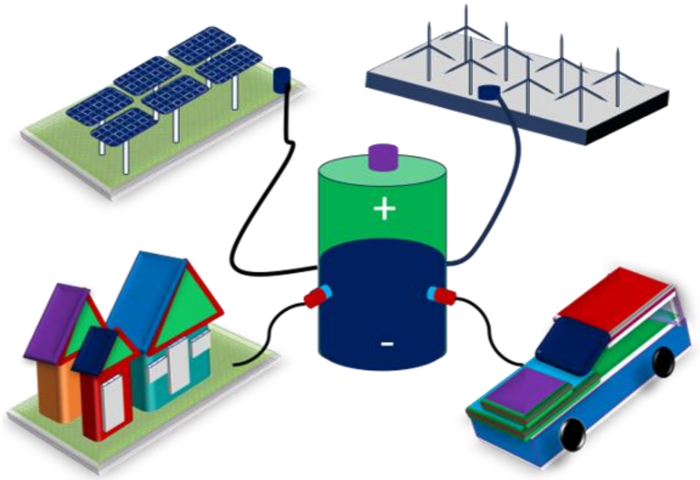

Figure 1.3 Schematic of Lithium-ion battery-based storage utilities.

1.5.1 Lithium-ion batteries (LIBs)

In the year 1970, the pioneering work of Stanley Whittingham, an English chemist basically kicks started the innovation in the world of batteries [53,54]. With the idea of constructing a Li ion-based battery, he used metallic lithium as the negative electrode and a chalcogenide based positive electrode TiS_2 to execute the first demonstration of a reversible battery. The two electrodes were separated by a porous separator soaked in an aprotic organic liquid electrolyte, typically containing a lithium-based salt. This kind of setup enabled reversible intercalation and deintercalation of lithium ions (Li^+) between the lithium metal and the chalcogenide materials. By utilizing lithium's special qualities such as a low molar mass ($6.94\ g\cdot mol^{-1}$), a low redox potential (Li^+/Li =-3.04 V against Standard Hydrogen Electrode (SHE)), and an extraordinarily high theoretical capacity of $3862\ mAh\cdot g^{-1}$, Whittingham proposed a groundbreaking idea [53]. These kinds of extraordinary results sparked commercial interest in lithium-based batteries, and Exxon and Moli Energy made an effort to commercialize these batteries. Even though early commercialization attempts showed the batteries' promise, there were serious safety issues, especially with the development of dendrites on the lithium metal during charging, which increased the risk of combustion and short circuiting. These shortcomings led to the halt of the expansion of the battery [55]. Ten years later in the 1980s, John Goodenough and his team transformed battery technology by introducing $LiCoO_2$ (LCO) as the positive electrode, which had a high redox potential of 3.7–3.9 V vs Li^+/Li. This allowed for non-lithiated materials to be used as the negative electrode [56]. Akira Yoshino further advanced this by using petroleum coke as the negative electrode in a Li-ion battery with LCO, leading to the first commercial Li-ion battery from Sony in 1991 [55, 57,58]. Their groundbreaking work earned Whittingham, Goodenough and Yoshino the Nobel Prize in Chemistry in 2019. Li-ion batteries, now dominated by graphite (0–0.25 V vs Li^+/Li), became commercially viable after the discovery of the solid electrolyte interphase (SEI), which ensures stable and reversible cycling [59,60]. Today, lithium-based metal oxides like nickel manganese cobalt and lithium iron phosphates are common positive electrodes, powering everything from electric vehicles to portable electronics, with energy densities up to 220 $Wh.kg^{-1}$ double that of nickel metal hydrate batteries [61,62]. In terms of market demand, in 2024 the global need of LIBs has crossed 1 terawatt hour per year [63,64].

1.5.2 Design and operational principle of Lithium-ion batteries (LIBs)

LIBs are basically a type of rechargeable battery which duly use Li ion as the primary charge carrier which intercalate reversibly in the electronically conducting host electrode material in order to generate and store electrochemical energy [65]. Being the lightest among all the existing metals, lithium produced largest specific energy density per weight. Also, the meteoric rise of LIBs since 1981 via rigorous breakthroughs leads to the significant enhancement of the volumetric energy and long cycling life stability. A typical LIBs comprise of graphite as negative electrode, a metal oxide or phosphate as cathode and a lithium salt in an organic electrolyte as electrolyte [66-68]. To prevent short circuiting of the electrodes, a separator is used. Both the electrodes are linked to the power circuit via two metal components known as current collectors. While operating, the electrodes swap their roles in order to facilitate subsequent charging and discharging. The positive electrode may consist of $LiCoO_2$ or $LiFePO_4$, whereas the negative electrode is usually graphite (with added silicon for increased capacity). Lithium hexafluorophosphate dissolved in organic carbonates serves as the electrolyte. During discharge, the anode (negative electrode) undergoes oxidation, releasing lithium ions and electrons, while the cathode (positive electrode) undergoes reduction. Electrons flow through the external circuit and lithium ions move through the electrolyte. This process is reversed during charging, when the cell must store chemical energy using external electrical energy. As the lithium ions moves back and forth via the electrodes during the energy generation process, these LIBs are also known as rocking chair or swing batteries [69,70].

1.5.3 Concerns associated with LIBs

In order to sustain with the present demand, batteries have to go past various factors like cost effectiveness, durability and most importantly safety. Despite their domination and the widespread use in powering everything from smartphones and laptops to electric vehicles (EVs) and renewable energy storage, LIBs are still far from being flawless and present a range of challenges across safety, performance, environmental, and resource sustainability [71]. The first and foremost limitation of LIBs is their thermal instability. The malfunctioning of any one internal component of the LIB cell leads to failure of these batteries leading to generation of heat. For example, if the separator gets dismantled due to some unwanted reason, the cell will undergo uncontrolled chemical reaction resulting in profound heat generation [72]. In normal conditions also, LIBs generate significant amount of heat as a result of the joule heat and the chemical energy generated. These energies are produced due to shuffling of Li^+ ions during each charge discharge cycle [73]. Other external factors such as overcharging can destabilize the battery's internal chemistry or short circuits, that lead to rapid discharge and excessive heat. These factors fuel the thermal mis-management of the LIB battery operation leading to uncontrolled heat buildup, potentially resulting in fires or explosions [74]. While modern devices include protections against these events, such as built-in charging circuits and thermal sensors, malfunctioning or improperly designed batteries may still pose significant risks. Moreover, the limited lifespan of LIBs, typically lasting only for 300 – 500 full charge/ discharge cycles before their energy storage capacity begins to degrade. The most annoying thing is that due to the undergoing internal chemical reactions, the degradation is bound to happen even if the battery is not in use [75-77]. In addition to these, the temperature sensitiveness upon exposure to fluctuating environmental conditions cause internal electrolyte to break down that reduce efficiency and overall capacity [78]. Another pressing concern is the environmental impacts of lithium-ion batteries. The extraction of key raw materials like lithium, cobalt, and nickel can have severe detrimental effects in the environment, from habitat destruction and water contamination to human rights violations [79,80]. The demand for these materials, mediated by the rapidly growing electric vehicle market and consumer electronics, is putting pressure on supply chains, which also lead to concerns about resource depletion. While battery recycling is a viable solution, the technology to execute these batteries recycling procedures efficiently is still in its infancy, resulting in low recovery rates and contributes to rapidly growing electronic waste problem [81]. Furthermore, many of the materials in lithium-ion batteries are difficult and costly to extract and reuse, making the environmental impact of their disposal a daunting task. As lithium-ion batteries continue to be essential for modern life, the increasing strain on global resources and supply chains raises significant concerns about their future availability [82]. To address these challenges, extensive research is underway to improve battery life, develop safer chemistries, enhance recycling technologies and find alternative materials.

1.6. Aqueous monovalent and multivalent energy storage systems

Exploration of safe, feasible and cost-effective storage solution bears utmost significance in order to mitigate pressing energy related global solutions. In this context aqueous monovalent and multivalent energy storage systems are gaining increasing attention in the field of energy storage, especially as the demand for sustainable, safe, and cost-effective alternatives to traditional lithium-ion batteries rises. These systems utilize aqueous electrolytes, which consist of water-based solutions, providing inherent safety advantages over non-aqueous systems, such as reduced risks of flammability and toxicity [83]. Among the monovalent ion-based batteries, LIBs are the most practical ones while other batteries like sodium ion batteries (SIBs), potassium ion batteries (PIBs) are also attaining widespread attention. The first prototype aqueous lithium-ion battery was demonstrated in the year 1994 by Prof. Jaff Dahn and coworkers [84]. In this particular battery, 5 M $LiNO_3$/1 mM LiOH aqueous solution was used as an electrolyte whereas the system used $LiMn_2O_4$ as cathode and VO_2 as anode. This cell exhibits a discharge voltage of 1.5 V and an energy density of 175 $Whkg^{-1}$. Thereafter, ample number of electrode materials such as $LiFePO_4$, $LiMnPO_4$, $LiNiPO_4$, and other doped polyanionic compounds are utilized for aqueous rechargeable lithium-ion batteries. In the year 2009, sodium based aqueous storage batteries were introduced where depiction of reversible insertion / de-insertion of Na^+ ion in $NaMnO_2$ electrode mediated by Na_2SO_4 aqueous solution was demonstrated [85]. In 2010, K^+ intercalation was demonstrated in $K_{0.27}MnO_2{\sim}0.6H_2O$ using K_2SO_4 aqueous electrolyte. Later, nickel hexacyanoferrate, a prussian blue analogue, was proposed as a cathode for potassium-ion batteries (PIBs) with a 1 M KNO_3 electrolyte, retaining 66% of its capacity at a high current rate [86]. Similarly, multivalent energy storage systems, which use divalent (e.g., Ca^{2+}, Mg^{2+}, Zn^{2+}) or even trivalent (e.g. Al^{3+}) ions as charge carriers, have the potential to offer higher theoretical energy densities. This is basically due to their capability to transfer more than one electron per cation electrochemistry [87]. In the year 2017, Chen et. al demonstrated a full Mg ion based aqueous battery using polyamide // nickel hexacyanoferrate redox couple in 1 M $MgSO_4$ electrolyte [88]. The breakthrough in the Ca^{2+} ion utilizing CuHCF electrode in a half cell set up using 8.37 M $Ca(NO_3)_2$ aqueous electrolyte also came in that year itself [89]. Similarly aqueous Zn ion batteries are also gaining lots of attention in terms of large-scale production due to their low redox potential (-0.76 V vs standard hydrogen electrode (SHE)) and high overpotential towards hydrogen evolution. In the past three years, progress in zinc ion batteries, particularly aqueous Zn–MnO_2 batteries, has been pushed by advancement in electrolyte technologies like salt-concentrated, hydrogel, pH-adjusted solutions [90]. This is why research on aqueous rechargeable batteries have attained widespread attention considering their alluring features like safety, cost effectiveness, environment amiability, high capacity and rate capability. Many aqueous based battery chemistries, once difficult to pursue are now becoming a feasible option due to the introduction of new electrode materials in this area. The flammability and better heat management in the aqueous batteries make them a clean substitute for the other existing nonaqueous energy storage devices as water can dissipate and absorb heat more effectively [91,92]. Moreover, in multivalent storage systems, their capability to transport more than one electron per cation facilitates higher capacity per unit weight or volume. In addition, the high ionic conductivity of aqueous electrolyte in comparison to the nonaqueous electrolytes stimulates smoother ion transport and provides low internal resistance leading to high energy and power density. This enhances the portability of these kinds of devices as higher amount of energy can be stored in a limited space [93]. The high concentration of water in aqueous electrolyte influences various parameters like hydration number, Stokes radius or hydrated radius etc. which further impact the solvation chemistry and ionic conductivity enhancing the battery dynamics. The high dielectric constant of water basically enhances the solvation or hydration energy which translates the improvement of solvation and desolation processes in the aqueous multivalent ion-based electrolytes [94]. Furthermore, aqueous electrolyte helps in countering solid diffusion concerns via shielding the multivalent ion charge of the multivalent metal cations are basically hydrated in aqueous media which helps them in withstanding the electrostatic repulsion between them and the host materials providing faster charge discharge kinetics with high rate of efficiency [95]. The lower overpotential in aqueous electrolyte reduces the energy loss during the electrochemical reactions that results in a minimized voltage drop which occurs due to internal resistance of the electrolyte. The lower overpotential also improves the coulombic efficiencies allowing minimal side reactions during cycling. This basically translate into higher energy efficiency along with reduced heat generation during subsequent cycling. In addition to these features, these systems are free from moisture control, sophisticated working environment and battery management issues which are an integral part of non-aqueous based energy storage devices [96,97].

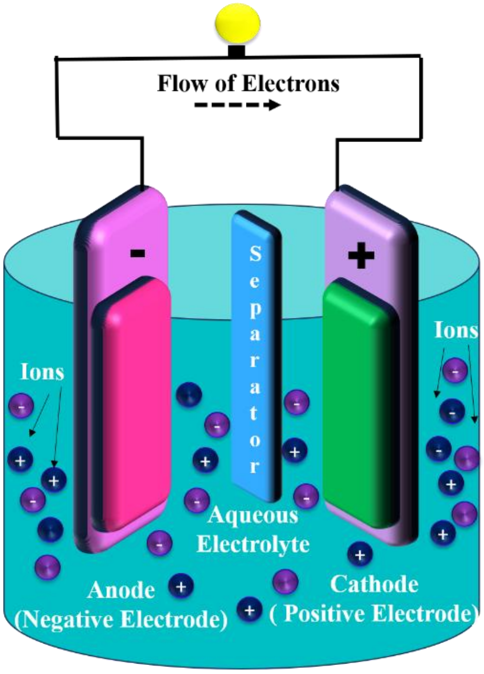

Figure 1.4 Schematic representation of an aqueous battery.

1.6.1 Aqueous Potassium ion batteries (APIBs)

Aqueous potassium ion batteries have sculptured increasing attention in the family of aqueous rechargeable batteries due to some of the fascinating features. The working principle of APIBs are similar with that of the rocking chair mechanism available in lithium-ion electrochemistry. During the charging process K^+ ion moves from the cathode and get inserted into the anode followed by release of electrons while the reverse happens in discharging of the electrode [98]. Moreover, the abundance of Potassium (K) is way larger than that of Lithium (Li) i.e. (approx. 2.09 % of earth crust by weight) which makes these raw materials cheaper in comparison to Li. The low standard reduction potential of K^+/K (-2.936 V vs. E°) leads to high potential energy density [99]. One of the striking features of K^+ is its low Lewis acidity which results in its low interaction with the organic solvents. Also, K forms the lowest solvated or Stokes radius in an aqueous solvent which basically provide enhanced diffusion rate of APIBs [100]. These kinds of features make APIBs a viable candidate for the beyond lithium-ion battery technologies. In the year 1978 itself, the first demonstration of APIBs using Prussian blue analogues was illustrated by Neff and coworkers, although a rapid exponential growth has been witnessed since 2017 [101]. A systematic study was performed from the group of Chales and coworkers where they have investigated a disordered vanadium oxide for APIBs [102]. In order to assemble the APIBs, the electrode materials play an important role. The redox potential of the electrode materials has to be in the range of electrolysis potential of water in order to restrict the electrode to electrolyze the water. Also, the large size of K^+ ions makes construction of APIBs more difficult [103]. Among various electrodes materials prussian blue analogues (PBAs), metal oxide and sulfide-based materials, Mxenes and commonly used carbon-based materials are widely investigated for APIBs [104-105]. Moreover, it is a known fact that defects may restrict the overall performance of the material by trapping the inserted ions and decreasing the active surface area. In terms of structural modification to enhance the overall performance, Zhu et al. described a low defect containing PBA for APIBs. In addition, doping Co into the FeHCF structure was also attempted in order to restore the material dissolution of PBAs in APIBs [106]. Furthermore, various polyanionic compounds and metal oxides are also explored in the field of APIBs. In the year 2014, a study on $Na_3V_2(PO_4)_3$ was reported as a electrode material for APIBs in K_2SO_4 electrolyte [107]. Co et al. described $KVPO_4$ in a super concentrated electrolyte for APIBs. Coming to various metal oxides that was explored for APIBs [108], Qu et al. reported the electrochemical performance of V_2O_5. (0.6) H_2O in K_2SO_4 aqueous electrolyte [109]. Mxenes are another class of electrode material which was explored recently. The group of Liang and coworkers have explored different Mxenes like Nb_2C, Ti_2C, and Ti_3C in order to illustrate K^+ ion electrochemistry for APIBs and the systems show 90% capacity retention up to 20000 cycles [110]. Although APIBs have made notable strides in recent years, sustained efforts are still required to reach true commercial viability. These innovations must counter the inherent limitations of aqueous electrolytes and the feasibility of various electrode materials in APIBs, while also investigating proper dissolution free electrode materials that could significantly improve energy and power density.

1.6.2 Aqueous Aluminium ion batteries (AAIBs)

In the present global arena of rechargeable batteries, aqueous aluminium ion batteries are becoming the subject of enormous interest due to some of the exciting features they offer. There are two types of Al ion-based configuration for AAIBs, one which directly uses Al metal as anode in combination with any type of Al ion conducting host electrode material called Al metal battery in an aqueous Al^{3+} ion conducting electrolyte and the second type resembles with the rocking chair mechanism of LIBs where both the electrode can reversibly host Al^{3+} ion in an aqueous electrolyte [111,112]. As discussed above, their ability to transfer more than one electron per cation makes aqueous aluminium ion batteries (AAIBs) appealing and unique in the context of other existing multivalent ion-based energy storage devices. All these metals are environment friendly and easily available which makes them feasible for use in the energy storage devices. Owing to these facts, aqueous rechargeable batteries based on aluminium ion are now being highly explored and are gaining widespread attention in the rechargeable battery arena [113]. The primary advantages of the aqueous aluminium ion batteries (AAIBs) lie in the fact that they are very cost effective, safe to operate and non-flammable. Also, the ability of aluminium to exchange three redox electrons during the electrochemical process makes them capable of delivering high theoretical volumetric capacity (8046 mAh cm^{-3}), which is much higher in comparison to the lithium cells (2062 mAh cm^{-3}) and other existing metal ion batteries [114]. This infers aluminium ion batteries to be smaller in size as energy densities of these batteries are in higher side. Most importantly aluminium is the 3rd most abundant element in the earth crust and has a very reliable gravimetric capacity of 2980 $mAhg^{-1}$ [115,116]. Also, the inertness of the aluminium metal facilitates its safe operation as anode in the aluminium metal battery with a suitable cathode in comparison to other metals like lithium, sodium etc. [117]. Irrespective of any advantages, the foremost important challenge for the development of AAIBs are to develop library of proper Al^{3+} ion host electrode material. The initial reports on aqueous Al ion battery were provided by Liu et al. where they have demonstrated TiO_2 based electrode material in Al_2SO_4 electrolyte in the year 2015 [118]. They procured a discharge capacity of 75 $mAhg^{-1}$ in $AlCl_3$ electrolyte. The work was carry forwarded by Holland et al. where they have procured a long-term stable cycling behaviour [119]. Kazazi et al. further improved the work and got a reversible discharge capacity of

180 mAhg^{-1} a current density of 50 mAg^{-1} [120]. Besides these, V_2O_5 was also explored as a feasible electrode material for AAIBs [121]. Pang and the coworkers developed an AAIB by combining Al metal as anode and $VOPO_4.2H_2O$ as cathode which exhibit a discharge plateau of 0.9 V. $VOPO_4$ was also studied by Wang et al in the year 2015 to construct a flexible hydrogel-based electrolyte for AAIBs which can sustain up to 2800 cycles with a quite lower capacity fading behaviour [122]. Another exciting assembling of AAIB was executed by Jiang and coworkers based on $Al_{82}Cu_{18}$ and Al_xMnO_2 as the cathode and the anode respectively [123]. Zhao and coworkers explored MnO_2 as cathode material for AAIBs [124]. Joseph et al. illustrated K-rich MnO_2 in aluminium ion conducting electrolytes [125]. $FeVO_4$ was also investigated by the group of Kumar et al. for AAIBs [126]. Prussian blue analogues are another class of electrode material which are also explored for AAIBs. In the year 2018 Holland et al. explored copper hexacyanoferrate in a mixture of $AlCl_3$ and KCl electrolyte [127]. Wang et al. executed a full aqueous Al ion cell with CuHCF positive electrode and MoO_3 negative electrode in the year 2019 [128]. MoO_3 is another transition metal-based electrode material which was explored for the first time from our group [129]. Similarly, WO_3, $LiMn_2O_4$, vanadyl ethelene glycolate (VEG), $LiFePO_4$, a particular class of mxenes, $MoTe_2$ are some of the other examples where Al ion insertion behavior was investigated from our group [130-135].

1.6.3. **Challenges ahead with aqueous batteries**

In-spite of such advantages, a prominent gap can be witnessed between aqueous batteries and the conventional LIBs in terms of delivering high energy density which basically prohibits aqueous batteries to scale in terms of large-scale production [136]. This kind of low energy density is primarily due to low operating voltage which is basically due to narrow operational potential window. Beyond a certain voltage, the aqueous electrolytes instigate oxygen and hydrogen evolution as a result of splitting of water. This kind of reaction basically consumes a large portion of electrons produced in the electrode surface resulting in low coulombic efficiency of the cell. Also, the shorter lifespan of these batteries accompanied by electrode material dissolution hampers the long terms cycling stability of these batteries [137]. Moreover, the corrosion and parasitic side reactions undergoing in the cell due to the reaction of electrode material and the electrolyte increases the instability of these batteries. Corrosion is a major parasitic reaction in strong acidic and alkaline solutions which basically fuels concentration change and irreversible consumption of water in the aqueous electrolyte. The dendrite growth associated with these reactions also adversely affects the full potential of these aqueous batteries detreating the cycling performances [138]. The phase transition associated with the water used in these electrolytes due to temperature variation restricts their wide range applicability. The multivalent systems also counter significant challenges, including slower ion diffusion due to the larger size of the divalent and trivalent ions and the greater electrostatic interactions they experience in comparison to monovalent ions. This slower diffusion can lead to lower charge and discharge rates, which is a major limitation for practical applications such as fast-charging devices or electric vehicles [139]. Therefore, this thesis evaluates the possibilities of various feasible electrode materials in aqueous K^+ and Al^{3+} storage systems along with various strategies to enhance its electrochemical performance.

1.7 Scope and Structure of the Thesis

The prime motivation of this thesis is to explore various aqueous based electrochemical energy storage systems. As discussed above, rechargeable batteries that use aqueous electrolytes are of great interest and have been heavily explored in the present scenario. With the befitting advantages aqueous batteries provides, monovalent and multivalent ion electro chemistries are subject for immense investigation from the research community. The scope of the thesis covers the exploration of two key approaches: identification of proper electrode materials and suitable optimization strategies aimed at improving their performance, scalability and sustainability for aqueous K^+ and Al^{3+} ion-based storage systems. These efforts provide paramount scope in terms of enhancing efficiency, safety and durability of the aqueous storage solutions.

1.8 Objectives of the thesis and overview

Based on the aforementioned aspects, following objectives are formulated:

1. Synthesis and structural investigations of carbonaceous, bismuth, niobium, and molybdenum-based electrode materials.
2. Electrochemical investigations to find the feasibility of K^+ ion and Al^{3+} ion storage.
3. Fundamental understanding of the electrochemical ion storage processes.

1.9 Choosing electrodes for aqueous batteries

In spite of tremendous research efforts on the development of proper electrode materials, the scalability of aqueous K^+ and Al^{3+} ion-based storage systems are still in its infancy in terms of long-term cycling performance to compete with the non-aqueous storage devices. From the above discussions, it is clear that monovalent and multivalent ion insertion leads to drastic structural and morphological transformation of the electrode material which leads to material dissolution, degrading the cycling performances. It is quite challenging to develop electrode materials feasible for aqueous electrolytes due to the limited thermodynamic stability of water as discussed earlier. The improper electrode can even instigate electrolyte decomposition, leading to self-discharge caused due to irreversible reaction in the electrolyte. Therefore, the thesis explores various forms of electrode materials like carbon-based materials, bismuth-based materials and finally some molybdenum-based electrode materials in order to explore their potential in K^+ and Al^{3+} ion-based storage devices in a feasible stability range of aqueous electrolytes. A brief literature review of the investigated electrode materials is provided below.

1.9.1 Carbon based materials

From the beginning of the inception of rechargeable batteries, carbon-based materials have been attaining widespread attention due to their various unique properties like high conductivity, large specific surface area, lightweight nature, flexibility, and abundance. Among the most widely used carbon-based materials graphite serves as the primary anode material in lithium-ion batteries since its commercialization by SONY in the year 1991. Since then, graphite has been a topic of immense interest in the fields of electrochemical energy storage. The unique layered structure of graphite makes it favorable for efficient intercalation and de-intercalation of lithium ions during the charge and discharge cycles [141]. Beyond graphite, other carbon-based materials like graphene, a single layer of carbon atoms arranged in a two-dimensional lattice, and carbon nanotubes, are being explored for use in next-generation batteries [142]. These materials offer superior conductivity, mechanical strength, and the potential for higher capacity due to their unique nanostructures. Since its discovery from the group of Novoselov et al., graphene has attracted huge attention in its use in industrial applications [143]. Graphene has a tensile strength of 125 GPA which depicts its superior mechanical integrity. Furthermore, various other characteristics like high surface area, high electrical conductivity etc. makes graphene extremely beneficial in its applicability in energy storage. Graphene can be used in lithium-ion batteries to improve both the anode and cathode materials. It can be combined with other materials, such as silicon, to create composite materials that offer higher capacity and faster charging times than traditional graphite anodes. Graphene also improves conductivity, which helps with faster electron and ion movement during the charge/discharge cycles, leading to faster charging and discharging times [144].

Another important member of the family is carbon nanotubes (CNT) which are also explored in electrochemical energy storage. CNTs also possess various extraordinary characteristics like high specific surface area, carrier mobilities and electrical conductivities which allow their application in energy storage devices. Similar to graphene, there are ample number of studies which explores different CNT based nanocomposites as electrode materials to enhance the cycling performances [145,146]. The group of Zhu and coworkers studied TiO_2 and superlined CNT as a flexible anode for lithium-ion batteries and procured a long cycling stability at a current rate of 60 C [147]. Han et al. synthesized a $Li_5Cr_7Ti_6O_{25}$ and CNT based nanocomposites using a sol gel method which shows impressive electrochemical performance [148].

1.9.2 Bismuth based Chalcogenides

Recently bismuth-based electrode materials have been widely explored to be the electrode material for various alkali metal ion batteries in the wake of some great extraordinary structural and morphological configuration they exhibit. The large interlayer spacing and the stable structure of bismuth-based materials even allows some large sized alkali metal ion like sodium ions to get inserted and extracted without much structural disintegration of the parental structure. This feature basically facilitates conversion type reactions mechanism which forms a range of stable microstructures leading to a high theoretical capacity, although the cyclic stability is somewhat compromised [149-151]. There are multiple reports where lithium and sodium ion insertion/de-insertion have been illustrated. The first reported study for metallic bismuth as electrode was performed by the Tarascon group where they have demonstrated electrodeposited nanosized Bi particles for lithium-ion storage [151]. Moreover, Omori et al. also studied spherical bismuth nanoparticles for LIBs [152]. Recently sodium ion electrochemistry has been explored in bulk Bi metal using a $NaPF_6$/diglyme electrolyte, where a stable capacity over 400 $mAhg^{-1}$ with a prolong cyclic stability have been achieved [153]. Similarly various studies have been conducted to explore the sodium ion electrochemistry in metallic bismuth electrodes [154-160]. Bismuth-based chalcogenides are another important class of compounds which have been investigated widely in recent times. Lu et al. demonstrated a Bi_2S_3/graphene composite electrode for sodium ion storage mechanism [160]. The conversion and intercalation type reaction in Bi_2S_3 after sodium insertion have been further confirmed by Sun et al. where they have demonstrated formation of $Na_xBi_2S_3$ followed by a phase transition to Bi phase [161]. Firodiponti and coworkers first demonstrated an in situ Bi_2O_3/ Ni foam electrodes for lithium storage [162]. A Bi_2O_3/ Bi_2S_3 hetero structure was reported by Liu et al. via partial sulfurization of Bi_2O_3 for LIBs [163]. In addition to these materials, Bismuth based oxyhalides and Mult compound metal oxides are also gaining a lot of attention for LIBs and SIBs. Zhang et al. demonstrated an ultra-thin BiOCl nanosheets for sodium ion batteries with an initial capacity of 1050 $mAhg^{-1}$ [164]. There are several reported studies on BiOBr and BiOI where these kinds of mechanism have been reported [165,166]. Although the electrochemical performance in these electrodes was somewhat compromised, there is scope for improvement. Moreover, Fang et al. studied $BiVO_4$ nanowire arrays for sodium ion storage with a very stable cycling capacity of 400 $mAhg^{-1}$ [167]. Durai et al. investigated $BiFeO_3$ nanoparticles to explore it as an anode material for sodium ion storage [168]. Although there are ample number of studies for these kind of materials in sodium and lithium-based energy storage devices, the aluminium ion storage behavior in these kinds of bismuth-based materials is yet to be fully explored. Nandi et al. has illustrated the aluminium storage behavior in Bi_2O_3 nanostructures and have accomplished a discharge capacity over 100 $mAhg^{-1}$ with a 99% coulombic efficiency [169]. Again, the same group has conducted study on the aqueous aluminium ion charge storage phenomena in BiOCl utilizing varying current collectors to sustain a stable cycling behavior [170].

1.9.3 Molybdenum based materials

In the quest for next generation electrode materials for aqueous batteries, molybdenum (Mo) based electrodes also garnered ample attention due to their unique physical and chemical advantages like structural integrity, large theoretical capacity, low toxicity and ease of handling [171-174]. It was found that molybdenum and oxygen can construct octahedral structure which facilitates formation of layered and tunnel structures. These structures particularly smoothen electrochemical ion insertion during battery cycling as a wide range of host cations can accommodate in the crystal structure [172]. In addition to that, Mo based material possesses variable oxidation states which facilitates enhanced electrochemical reaction, thus enhancing the performance. Due to this unique feature, Mo based electrode materials deliver much higher electrochemical performance in comparison to the carbon-based electrode materials. Mo based materials like molybdenum trioxide (MoO_3), molybdenum disulfide (MoS_2) etc. are easily tunable which also help to retain the structural integrity of the electrode material [173]. Recently MoS_2 microspheres have been explored as a cathode material for non-aqueous aluminum ion batteries in a mixture of 1 M $AlCl_3$/1-ethyl-3 methylimidazolium chloride ([EMIm]Cl) ionic liquid in the ratio of 1.3:1. It was reported that with this kind of set up a stable capacity of 66.7 $mAhg^{-1}$ over 100 cycles was achieved [174]. Yang et al. developed a MoS_2/ carbon nanofiber composite in order to enhance the specific capacity and have achieved a discharge capacity of 126 $mAhg^{-1}$ at a current density of 100 mAg^{-1} over 200 cycles [175]. A novel phase engineering approach was reported by Tan et al. where a composite of MoS_2 and reduced graphene oxide was prepared via hydrothermal method. This kind of structure provides ample number of active sites for Al^{3+} ion diffusion into the structure which basically improves the storage capacity. The reported capacity for this work is 150 $mAhg^{-1}$ over 100 cycles at a current density of 1 Ag^{-1} [176]. Another approach of preparing MoS_2 in Mxene network was provided by the same group which significantly improved the aluminium ion charge storage capacities as a stable capacity of 224 $mAhg^{-1}$ was attained [177]. MoO_3 is another very important example of Mo based materials with significant optical and electronic functionalities which is extensively studied for their use in various applications like sensors, catalysis, electronics and energy storage etc. [178,179]. Recently the group of Wang and coworkers demonstrated another approach by incorporating an inorganic layer of TiO_2 on α-MoO_3 which significantly impedes the material dissolution problem [180]. The group of Choi and Kang grew α-MoO_3 on crumpled graphene sheet via spray pyrolysis followed by a thermal treatment. This modification significantly enhanced cycling behaviour as a very high discharge capacity of 975 $mAhg^{-1}$ was obtained for 90 cycles [181]. Similarly, Lou and coworkers prepared α-MoO_3 nanobelts to get a very high discharge capacity of 730 $mAhg^{-1}$ at a current rate of 0.2 C with a modified sodium carboxymethyl cellulose [182]. The group of Hassan and coworkers constructed carbon coated α-MoO_3 nanobelts to procure a discharge capacity of 1000 $mAhg^{-1}$[183]. Dillon et al. also investigated Li ion insertion behavior in MoO_3 prepared via a hot wire chemical vapour deposition method [184]. Our group also demonstrated MoO_3 for aqueous Al-ion batteries. An effective strategy of electrolyte engineering via using diglyme and water mixture was put forwarded from our group [185]. Similarly, gel polymer electrolytes are also illustrated to construct a Zn//α-MoO_3 aqueous cell in Zn^{2+} ion conducting electrolytes for aqueous Zn-ion batteries [186]. Most recently a unique strategy of creating oxygen vacancy and coating of a Al_2O_3 protective layer to modify interface layers of MoO_3 was executed by Liu and coworkers in order to get a stable cycling performance with enhanced surface reactivity [187].

1.9 References

[1] Crabtree G. Perspective: The energy-storage revolution. *Nature*. 526(7575): S92, 2015.

[2] Energy Storage Association, 35x25 A vision for energy storage, 2017.

[3] https://www.un.org/en/climatechange

[4] https://unfccc.int/event/cop-21

[5] https://unfccc.int/process-and-meetings/the-paris-agreement

[6] https://www.activesustainability.com/climate-change/a-plan-for-carbon-neutrality-by-2050.

[7] https://www.iea.org/topics/global-energy-crisis

[8] Guan Y., Yan J., Shan Y., Zhou Y., Hang Y, Li R., Liu Y., Liu B., Nie Q., Bruckner B., and Feng K. Burden of the global energy price crisis on households. *Nature Energy*, 8(3):304-16, 2023.

[9] Goldthau A., Tagliapietra S. Energy crisis: five questions that must be answered in 2023. *Nature*, 612(7941): 627-30, 2022.

[10] Tian J., Yu L., Xue R., Zhuang S., Shan Y. Global low-carbon energy transition in the post-COVID-19 era. *Applied Energy*. 307:118205, 2022.

[11] Larcher D., Tarascon J. M. Towards greener and more sustainable batteries for electrical energy storage. *Nature chemistry*.7(1):19-29, 2015.

[12] Gielen D., Gorini R., Wagner N., Leme R., Gutierrez L., Prakash G., Asmelash E., Janeiro L., Gallina G., Vale G., and Sani L. Global energy transformation: a roadmap to 2050, 2019.

[13] Dunn B., Kamath H., and Tarascon J. M. Electrical energy storage for the grid: a battery of choices. *Science*. 334(6058): 928-35, 2011.

[14] Larcher, D. and Tarascon, J. M. (2015). Towards greener and more sustainable batteries for electrical energy storage. *Nature chemistry*, *7*(1): 19-29, 2015.

[15] Ellabban, O., Abu-Rub, H. and Blaabjerg, F. Renewable energy resources: Current status, future prospects and their enabling technology. *Renewable and sustainable energy reviews*, 39: 748-764, 2014.

[16] Matos, C.R., Carneiro, J.F., and Silva, P. P. Overview of large-scale underground energy storage technologies for integration of renewable energies and criteria for reservoir identification. *Journal of Energy Storage*, 21: 241-258, 2019.

[17] Iqbal, M., Azam, M., Naeem, M., Khwaja, A.S., and Anpalagan, A. Optimization classification, algorithms and tools for renewable energy: A review. *Renewable and sustainable energy reviews*, 39: 640-654, 2014.

[18] Du, P., and Lu, N. *Energy storage for smart grids: planning and operation for renewable and variable energy resources (VERs)*. Academic Press, 2014.

[19] Moseley, P. T., and Garche, J. (Eds.). *Electrochemical energy storage for renewable sources and grid balancing*. *Newnes*, 2014.

[20] Hassan, Q., Hsu, C.Y., Mounich, K., Algburi, S., Jaszczur, M., Telba, A.A., Viktor, P., Awwad, E.M., Ahsan, M., Ali, B.M., and Al-Jiboory, A.K. Enhancing smart grid integrated renewable distributed generation capacities: Implications for sustainable energy transformation. *Sustainable Energy Technologies and Assessments*, 66 :103793

[21] Dunn, B., Kamath, H., and Tarascon, J. M. Electrical energy storage for the grid: a battery of choices. *Science*, *334*(6058): 928-935, 2011.

[22] Hevia-Koch, P., Wanner, B. and Kuwahata, R., Electricity grids and secure energy transitions. *IEA: Paris, Frence*, 2023.

[23] Weinand, J.M., Hoffmann, M., Göpfert, J., Terlouw, T., Schönau, J., Kuckertz, P., McKenna, R., Kotzur, L., Linßen, J. and Stolten, D. Global LCOEs of decentralized off-grid renewable energy systems. *Renewable and Sustainable Energy Reviews*, 183: 113478, 2023.

[24] Weinand, J.M., Scheller, F. and McKenna, R. Reviewing energy system modelling of decentralized energy autonomy. *Energy*, 203: 117817, 2020.

[25] Engelken, M., Römer, B., Drescher, M. and Welpe, I. Transforming the energy system: Why municipalities strive for energy self-sufficiency. *Energy Policy*, 98: 365-377, 2016.

[26] Wang, W., Yuan, B., Sun, Q. and Wennersten, R., Application of energy storage in integrated energy systems—A solution to fluctuation and uncertainty of renewable energy. *Journal of Energy Storage*, 52: 104812, 2022

[27] Dunn, B., Kamath, H. and Tarascon, J.M., Electrical energy storage for the grid: a battery of choices. *Science*, 334(6058): 928-935, 2011.

[28] Koohi-Fayegh, S. and Rosen, M.A., A review of energy storage types, applications and recent developments. *Journal of Energy Storage*, 27: 101047, 2020.

[29] Argyrou, M.C., Christodoulides, P. and Kalogirou, S.A., Energy storage for electricity generation and related processes: Technologies appraisal and grid scale applications. *Renewable and Sustainable Energy Reviews*, 94: 804-821, 2018.

[30] Olabi, A.G. and Abdelkareem, M.A., Energy storage systems towards 2050. *Energy*, 219:119634, 2021.

[31] Argyrou, M.C., Christodoulides, P. and Kalogirou, S.A., Energy storage for electricity generation and related processes: Technologies appraisal and grid scale applications. *Renewable and Sustainable Energy Reviews*, 94: 804-821, 2018.

[32] Larcher, D. and Tarascon, J.M., Towards greener and more sustainable batteries for electrical energy storage. *Nature chemistry*, 7(1): 19-29, 2015.

[33] https://www.energy.gov/eere/water/pumped-storage-hydropower.

[34] Yekini Suberu M, Wazir Mustafa M, Bashir N. Energy storage systems for renewable energy power sector integration and mitigation of intermittency. Renew Sustain Energy Reviews; 35:499–514, 2014.

[35] Goodenough, J.B., Electrochemical energy storage in a sustainable modern society. *Energy & Environmental Science*, 7(1): 14-18, 2014.

[36] Manthiram, A., Fu, Y. and Su, Y.S., In charge of the world: electrochemical energy storage. *The Journal of Physical Chemistry Letters*, 4(8):1295-1297, 2013.

[37] Yang, Z., Zhang, J., Kintner-Meyer, M.C., Lu, X., Choi, D., Lemmon, J.P. and Liu, J., Electrochemical energy storage for green grid. *Chemical reviews*, 111(5): 3577-3613, 2011.

[38] Gogotsi, Y. and Simon, P., True performance metrics in electrochemical energy storage. *Science*, 334(6058): 917-918, 2011.

[39] Xiao, B.H., Xiao, K., Li, J.X., Xiao, C.F. and Liu, Z.Q., Flexible Electrochemical Energy Storage Devices and Related Applications: Recent Progress and Challenge. *Chemical Science*: 2024.

[40] Ji, X., A paradigm of storage batteries. *Energy & Environmental Science*, 12(11): 3203-3224, 2019.

[41] Xu, Q. and Zhao, T.S., Fundamental models for flow batteries. *Progress in Energy and Combustion Science*, 49*:* 40-58, 2015.

[42] Guney, M.S. and Tepe, Y., Classification and assessment of energy storage systems. *Renewable and sustainable energy reviews*, 75: 1187-1197, 2017.

[43] Koohi-Fayegh, S. and Rosen, M.A., A review of energy storage types, applications and recent developments. *Journal of Energy Storage*, 27: 101047, 2020.

[44] Liu, W., Placke, T. and Chau, K.T., Overview of batteries and battery management for electric vehicles. *Energy Reports*, 8: 4058-4084, 2022.

[45] Tarascon, J.M. and Armand, M., Issues and challenges facing rechargeable lithium batteries. *nature*, 414(6861): 359-367, 2001.

[46] Goodenough, J.B. and Park, K.S., The Li-ion rechargeable battery: a perspective. *Journal of the American Chemical Society*, 135(4):1167-1176, 2013.

[47] Goodenough, J.B., Electrochemical energy storage in a sustainable modern society. *Energy & Environmental Science*, 7(1):14-18, 2014.

[48] Goodenough, J.B. and Park, K.S., The Li-ion rechargeable battery: a perspective. *Journal of the American Chemical Society*, 135(4):1167-1176, 2013.

[49] Goodenough, J.B., How we made the Li-ion rechargeable battery. *Nature Electronics*, 1(3): 204-204, 2018.

[50] Peters, J.F., Baumann, M., Zimmermann, B., Braun, J. and Weil, M., The environmental impact of Li-Ion batteries and the role of key parameters–A review. *Renewable and Sustainable Energy Reviews*, 67: 491-506, 2017.

[51] Barreras, J.V., Pinto, C., de Castro, R., Schaltz, E., Andreasen, S.J. and Araújo, R.E.Multi-objective control of balancing systems for li-ion battery packs: A paradigm shift? In 2014 *IEEE Vehicle Power and Propulsion Conference (VPPC)* (1-7). IEEE: 2014.

[52] Kennedy, B., Patterson, D. and Camilleri, S., Use of lithium-ion batteries in electric vehicles. *Journal of Power Sources*, 90(2): 156-162, 2000.

[53] Whittingham, M.S., Electrical energy storage and intercalation chemistry. *Science*, 192(4244): 1126-1127, 1976.

[54] Deng, D., Li-ion batteries: basics, progress, and challenges. *Energy Science & Engineering*, *3*(5): 385-418, 2015.

[55] Li, M., Lu, J., Chen, Z. and Amine, K., 30 years of lithium-ion batteries. *Advanced materials*, *30*(33): 1800561, 2018.

[56] Mizushima, K.J.P.C., Jones, P.C., Wiseman, P.J. and Goodenough, J.B., Li_xCoO_2 (0< x<-1): A new cathode material for batteries of high energy density. *Materials Research Bulletin*, *15*(6): 783-789, 1980.

[57] Yoshino, A., Sanechika, K. and Nakajima, T., Secondary battery Japanese patent no. 1989293, 1985.

[58] Ogawa, S., Profile of Akira Yoshino, Dr. Eng., and Overview of His Invention of the Lithium-ion Battery.

[59] Linsenmann, Fabian; Pritzl, Daniel; Gasteiger, Hubert A, "Comparing the Lithiation and Sodiation of a Hard Carbon Anode Using in Situ Impedance Spectroscopy". *Journal of the Electrochemical Society*. 168 (1): 010506, 2021.

[60] Nitta, N., Wu, F., Lee, J.T. and Yushin, G., Li-ion battery materials: present and future. *Materials today*, 18(5): 252-264, 2015.

[61] Manthiram, A., A reflection on lithium-ion battery cathode chemistry. *Nature communications*, 11(1): 1550, 2020.

[62] Okada, S. and Yamaki, J.I., Iron-Based Rare-Metal-Free Cathodes. *Lithium-Ion Rechargeable Batteries: Materials, Technology, and New Applications*: 53-66, 2009.

[63] https://www.statista.com/topics/2049/lithium-ion-battery-industry/

[64] https://www.iea.org/reports/batteries-and-secure-energy-transitions/executive-summary

[65] Chagas, L.G., Jeong, S., Hasa, I. and Passerini, S., Ionic liquid-based electrolytes for sodium-ion batteries: tuning properties to enhance the electrochemical performance of manganese-based layered oxide cathode. *ACS applied materials & interfaces*, 11(25): 22278-22289, 2019.

[66] https://www.ess-news.com/2024/12/20/annual-lithium-ion-demand-surpasses-1-twh-for-the-first-time/

[67] Li, A., Yuen, A.C.Y., Wang, W., De Cachinho Cordeiro, I.M., Wang, C., Chen, T.B.Y., Zhang, J., Chan, Q.N. and Yeoh, G.H., A review on lithium-ion battery separators towards enhanced safety performances and modelling approaches. *Molecules*, 26(2): 478, 2021.

[68] Thackeray, M.M., Thomas, J.O. and Whittingham, M.S., Science and applications of mixed conductors for lithium batteries. *MRS bulletin*, 25(3): 39-46, 2000.

[69] Zhu, P., Gastol, D., Marshall, J., Sommerville, R., Goodship, V. and Kendrick, E., A review of current collectors for lithium-ion batteries. *Journal of Power Sources*, 485: 229321, 2021.

[70] Xu, K., Nonaqueous liquid electrolytes for lithium-based rechargeable batteries. *Chemical reviews*, 104(10): 4303-4418, 2004.

[71] Bandhauer, T.M., Garimella, S. and Fuller, T.F., A critical review of thermal issues in lithium-ion batteries. *Journal of the electrochemical society*, 158(3): R1, 2011.

[72] Wang, Q., Jiang, B., Li, B. and Yan, Y., A critical review of thermal management models and solutions of lithium-ion batteries for the development of pure electric vehicles. *Renewable and sustainable energy reviews*, 64:106-128, 2016.

[73] Zhang, X., Li, Z., Luo, L., Fan, Y. and Du, Z., A review on thermal management of lithium-ion batteries for electric vehicles. *Energy*, 238: p.121652, 2022.

[74] Wakihara, M., Recent developments in lithium-ion batteries. *Materials Science and Engineering: R: Reports*, 33(4): 109-134, 2001.

[75] Chen, J., Recent progress in advanced materials for lithium-ion batteries. *Materials*, 6(1): 156-183, 2013.

[76] Ruiz, V., Pfrang, A., Kriston, A., Omar, N., Van den Bossche, P. and Boon-Brett, L., A review of international abuse testing standards and regulations for lithium ion batteries in electric and hybrid electric vehicles. *Renewable and Sustainable Energy Reviews*, 81: 1427-1452, 2018.

[77] Wu, X., Song, K., Zhang, X., Hu, N., Li, L., Li, W., Zhang, L. and Zhang, H., Safety issues in lithium-ion batteries: Materials and cell design. *Frontiers in Energy Research*, 7: 65, 2019.

[78] Peters, J.F., Baumann, M., Zimmermann, B., Braun, J. and Weil, M., The environmental impact of Li-Ion batteries and the role of key parameters–A review. *Renewable and Sustainable Energy Reviews*, 67: 491-506, 2017.

[79] Costa, C.M., Barbosa, J.C., Gonçalves, R., Castro, H., Del Campo, F.J. and Lanceros-Méndez, S., Recycling and environmental issues of lithium-ion batteries: Advances, challenges and opportunities. *Energy Storage Materials*, 37: 433-465, 2021.

[80] Baum, Z.J., Bird, R.E., Yu, X. and Ma, J., Lithium-ion battery recycling─ overview of techniques and trends, 2022.

[81] Ciez, R.E. and Whitacre, J.F., The cost of lithium is unlikely to upend the price of Li-ion storage systems. *Journal of Power Sources*, 320: 310-313, 2016.

[82] Ahn, H., Kim, D., Lee, M. and Nam, K.W., Challenges and possibilities for aqueous battery systems. *Communications Materials*, 4(1): 37, 2023.

[83] Li, W., Dahn, J.R. and Wainwright, D.S., Rechargeable lithium batteries with aqueous electrolytes. *Science*, 264(5162): 1115-1118, 1994.

[84] Qu, Q.T., Shi, Y., Tian, S., Chen, Y.H., Wu, Y.P. and Holze, R., A new cheap asymmetric aqueous supercapacitor: activated carbon//$NaMnO_2$. *Journal of Power Sources*, 194(2): 1222-1225, 2009.

[85] Qu, Q., Li, L., Tian, S., Guo, W., Wu, Y. and Holze, R., A cheap asymmetric supercapacitor with high energy at high power: Activated carbon//K0. 27MnO2· 0.6 H2O. *Journal of Power Sources*, 195(9): 2789-2794, 2010.

[86] Rong, Z., Malik, R., Canepa, P., Sai Gautam, G., Liu, M., Jain, A., Persson, K. and Ceder, G., Materials design rules for multivalent ion mobility in intercalation structures. *Chemistry of Materials*, 27(17): 6016-6021, 2015.

[87] Chen, L., Bao, J.L., Dong, X., Truhlar, D.G., Wang, Y., Wang, C. and Xia, Y., Aqueous Mg-ion battery based on polyimide anode and prussian blue cathode. *ACS Energy Letters*, 2(5): 1115-1121, 2017.

[88] Lee, C. and Jeong, S.K., A novel superconcentrated aqueous electrolyte to improve the electrochemical performance of calcium-ion batteries. *Chemistry Letters*, 45(12): 1447-1449, 2016.

[89] Fang, G., Zhou, J., Pan, A. and Liang, S., Recent advances in aqueous zinc-ion batteries. *ACS Energy Letters*, 3(10): 2480-2501, 2018.

[90] Pan, Z., Liu, X., Yang, J., Li, X., Liu, Z., Loh, X.J. and Wang, J., Aqueous rechargeable multivalent metal-ion batteries: advances and challenges. *Advanced Energy Materials*, 11(24): 2100608, 2021.

[91] Chao, D., Zhou, W., Xie, F., Ye, C., Li, H., Jaroniec, M. and Qiao, S.Z., Roadmap for advanced aqueous batteries: From design of materials to applications. *Science advances*, 6(21): 4098, 2020.

[92] Pan, Z., Liu, X., Yang, J., Li, X., Liu, Z., Loh, X.J. and Wang, J., Aqueous rechargeable multivalent metal-ion batteries: advances and challenges. *Advanced Energy Materials*, 11(24): 2100608, 2021.

[93] Jia, X., Liu, C., Neale, Z.G., Yang, J. and Cao, G., Active materials for aqueous zinc ion batteries: synthesis, crystal structure, morphology, and electrochemistry. Chemical Reviews, 120(15): 7795-7866, 2020.

[94] Zou, X. and Zhang, Y., Noble metal-free hydrogen evolution catalysts for water splitting. *Chemical Society Reviews*, 44(15): 5148-5180, 2015.

[95] Pan, Z., Liu, X., Yang, J., Li, X., Liu, Z., Loh, X.J. and Wang, J., Aqueous rechargeable multivalent metal-ion batteries: advances and challenges. *Advanced Energy Materials*, 11(24): 2100608, 2021.

[96] Shin, J., Lee, J., Park, Y. and Choi, J.W., Aqueous zinc ion batteries: focus on zinc metal anodes. *Chemical science*, 11(8): 2028-2044, 2020.

[97] Zhang, X., Xiong, T., He, B., Feng, S., Wang, X., Wei, L. and Mai, L., Recent advances and perspectives in aqueous potassium-ion batteries. *Energy & Environmental Science*, 15 (9): 3750-3774, 2022.

[98] Zhang, W., Liu, Y. and Guo, Z., high-performance potassium-ion batteries via advanced design strategies and engineering. *Science advances*, 5(5): 7412, 2019. Approaching

[99] Liang, G., Mo, F., Ji, X. and Zhi, C., Non-metallic charge carriers for aqueous batteries. *Nature Reviews Materials*, 6(2): 109-123, 2021.

[100] Neff, V.D., Electrochemical oxidation and reduction of thin films of Prussian blue. *Journal of the Electrochemical Society*, 125(6): 886, 1978.

[101] Charles, D., Page, K., Neuefeind, J. and Teng, X., March. Structural water engaged disordered vanadium oxide nanosheets for high-capacity aqueous K-ion storage. In *Abstracts of Papers of the American Chemical Society* (Vol. 255). 1155 16TH ST, NW, WASHINGTON, DC 20036 USA: AMER CHEMICAL SOC, 2018,

[102] Liu, Y., Tai, Z., Zhang, J., Pang, W.K., Zhang, Q., Feng, H., Konstantinov, K., Guo, Z. and Liu, H.K., Boosting potassium-ion batteries by few-layered composite anodes prepared via solution-triggered one-step shear exfoliation. *Nature communications*, 9(1): 3645, 2018.

[103] Zhou, A., Cheng, W., Wang, W., Zhao, Q., Xie, J., Zhang, W., Gao, H., Xue, L. and Li, J., Hexacyanoferrate-type Prussian blue analogs: principles and advances toward high-performance sodium and potassium ion batteries. *Advanced Energy Materials*, 11(2): 2000943, 2021.

[104] Wang, R.Y., Shyam, B., Stone, K.H., Weker, J.N., Pasta, M., Lee, H.W., Toney, M.F. and Cui, Y., Reversible multivalent (monovalent, divalent, trivalent) ion insertion in open framework materials. *Advanced Energy Materials*, 5(12): 1401869, 2015.

[105] Ma, C., Lin, C., Li, N., Chen, Y., Yang, Y., Tan, L., Wang, Z., Zhang, Q. and Zhu, Y., A High-Entropy Prussian Blue Analog for Aqueous Potassium-Ion Batteries. *Small*, 20(23): 2310184, 2024.

[106] Song, W., Ji, X., Zhu, Y., Zhu, H., Li, F., Chen, J., Lu, F., Yao, Y. and Banks, C.E., Aqueous Sodium-Ion Battery using a $Na3V_2(PO_4)_3$ Electrode. *ChemElectroChem*, 1(5): 871-876, 2014.

[107] Byeon, Y.W., Gong, M.J., Cai, Z., Sun, Y., Szymanski, N.J., Bai, J., Seo, D.H. and Kim, H., Effects of cation and anion substitution in $KVPO_4F$ for K-ion batteries. *Energy Storage Materials*, 57: 81-91, 2023.

[108] Qu, Q.T., Shi, Y., Li, L.L., Guo, W.L., Wu, Y.P., Zhang, H.P., Guan, S.Y. and Holze, R., $V_2O_5.0.6\ H_2O$ nanoribbons as cathode material for asymmetric supercapacitor in K_2SO_4 solution. *Electrochemistry Communications*, 11(6): 1325-1328, 2009.

[109] Liang, G., Li, X., Wang, Y., Yang, S., Huang, Z., Yang, Q., Wang, D., Dong, B., Zhu, M. and Zhi, C., Building durable aqueous K-ion capacitors based on MXene family. *Nano Research Energy*, *1*(1): 9120002, 2022.

[110] Stephanie, R., Park, C.Y., Shinde, P.A., Alhajri, E., Chodankar, N.R. and Park, T.J., Aqueous aluminum ion system: A future of sustainable energy storage device. *Energy Storage Materials*, 68: 103336, 2024.

[111] Das, S.K., Mahapatra, S. and Lahan, H., Aluminium-ion batteries: developments and challenges. *Journal of Materials Chemistry A*, 5(14): 6347-6367, 2017.

[112] Melzack, N. and Wills, R.G.A., A review of energy storage mechanisms in aqueous aluminium technology. *Frontiers in Chemical Engineering*, 4: 778265, 2022.

[113] Jia, B.E., Thang, A.Q., Yan, C., Liu, C., Lv, C., Zhu, Q., Xu, J., Chen, J., Pan, H. and Yan, Q., Rechargeable Aqueous Aluminum-Ion Battery: Progress and Outlook. *Small*, 18(43): 2107773, 2022.

[114] Zhang, Y., Liu, S., Ji, Y., Ma, J. and Yu, H., Emerging nonaqueous aluminum-ion batteries: challenges, status, and perspectives. *Advanced Materials*, 30(38): 1706310, 2018.

[115] Elia, G.A., Marquardt, K., Hoeppner, K., Fantini, S., Lin, R., Knipping, E., Peters, W., Drillet, J.F., Passerini, S. and Hahn, R., An overview and future perspectives of aluminum batteries. *Advanced Materials*, 28(35): 7564-7579, 2016.

[116] Shen, X., Sun, T., Yang, L., Krasnoslobodtsev, A., Sabirianov, R., Sealy, M., Mei, W.N., Wu, Z. and Tan, L., Ultra-fast charging in aluminum-ion batteries: electric double layers on active anode. *Nature communications*, 12(1): 820, 2021.

[117] Liu, S., Hu, J.J., Yan, N.F., Pan, G.L., Li, G.R. and Gao, X.P., Aluminum storage behavior of anatase TiO 2 nanotube arrays in aqueous solution for aluminum ion batteries. *Energy & Environmental Science*, 5(12): 9743-9746, 2012.

[118] Holland, A.W., McKerracher, R., Cruden, A. and Wills, R.G.A., TiO2 nanopowder as a high rate, long cycle life electrode in aqueous aluminium electrolyte. *Materials today energy*, 10: 208-213, 2018.

[119] Kazazi, M., Abdollahi, P. and Mirzaei-Moghadam, M., High surface area TiO2 nanospheres as a high-rate anode material for aqueous aluminium-ion batteries. *Solid State Ionics*, 300: 32-37, 2017.

[120] De, P., Halder, J., Priya, S., Srivastava, A.K. and Chandra, A., Two-dimensional V_2O_5 nanosheets as an advanced cathode material for realizing low-cost aqueous aluminum-ion batteries. *ACS Applied Energy Materials*, *6*(2): 753-762, 2023.

[121] Pang, Q., Yang, S., Yu, X., He, W., Zhang, S., Tian, Y., Xing, M., Fu, Y. and Luo, X., Realizing reversible storage of trivalent aluminum ions using VOPO4· $2H_2O$ nanosheets as cathode material in aqueous aluminum metal batteries. *Journal of Alloys and Compounds*, 885: 161008, 2021.

[122] Ran, Q., Shi, H., Meng, H., Zeng, S.P., Wan, W.B., Zhang, W., Wen, Z., Lang, X.Y. and Jiang, Q., Aluminum-copper alloy anode materials for high-energy aqueous aluminum batteries. *Nature Communications*, 13(1): 576, 2022.

[123] Chen, C., Shi, M., Zhao, Y., Yang, C., Zhao, L. and Yan, C., Al-Intercalated MnO2 cathode with reversible phase transition for aqueous Zn-Ion batteries. *Chemical Engineering Journal*, 422: 130375, 2021.

[124] Joseph, J., Nerkar, J., Tang, C., Du, A., O'Mullane, A.P. and Ostrikov, K., Reversible Intercalation of Multivalent Al^{3+} Ions into Potassium-Rich Cryptomelane Nanowires for Aqueous Rechargeable Al-Ion Batteries. *ChemSusChem*, 12(16): 3753-3760, 2019.

[125] Kumar, S., Satish, R., Verma, V., Ren, H., Kidkhunthod, P., Manalastas Jr, W. and Srinivasan, M., Investigating $FeVO_4$ as a cathode material for aqueous aluminum-ion battery. *Journal of Power Sources*, 426:151-161, 2019.

[126] Holland, A., Kimpton, H., Cruden, A. and Wills, R., CuHCF as an electrode material in an aqueous dual-ion Al3+/K+ ion battery. *Energy Procedia*, 151:69-73, 2018.

[127] Wang, P., Chen, Z., Ji, Z., Feng, Y., Wang, J., Liu, J., Hu, M., Wang, H., Gan, W. and Huang, Y., A flexible aqueous Al ion rechargeable full battery. *Chemical Engineering Journal*, 373: 580-586, 2019.

[128] Lahan, H. and Das, S.K., Al^{3+} ion intercalation in MoO_3 for aqueous aluminum-ion battery. Journal of power sources, 413: 134-138, 2019.

[129] Lahan, H. and Das, S.K., Reversible Al^{3+} ion insertion into tungsten trioxide (WO_3) for aqueous aluminum-ion batteries. *Dalton Transactions*, 48(19): 6337-6340, 2019.

[130] Nandi, S. and Das, S.K., An electrochemical study on LiMn2O4 for Al^{3+} ion storage in aqueous electrolytes. *Physical Chemistry Chemical Physics*, 23(35): 19150-19154, 2021.

[131] Nandi, S., Yan, Y., Yuan, X., Wang, C., He, X., Li, Y. and Das, S.K., Vanadyl ethylene glycolate: A novel organic-inorganic electrode material for rechargeable aqueous aluminum-ion battery. *Solid State Ionics*, 389: 116085, 2023.

[132] Sarmah, D. and Das, S.K., Elucidating the Al^{3+} ion electrochemical behaviour of LiFePO4. *Bulletin of Materials Science*, 46(1): 43, 2023.

[133] Sarmah, D., Goswami, T.K. and Das, S.K., Aqueous electrolyte-mediated Al^{3+} ion storage in electrochemically treated Ti_3AlC_2. *Bulletin of Materials Science*, 47(1): 23, 2024.

[134] Nandi, S., Yan, Y., Yuan, X., Wang, C., He, X., Li, Y. and Das, S.K., Investigation of reversible metal ion (Li^+, Na^+, Mg^{2+}, Al^{3+}) insertion in $MoTe_2$ for rechargeable aqueous batteries. *Physical Chemistry Chemical Physics*, 25(20): 13833-13837, 2023.

[135] Ahn, H., Kim, D., Lee, M. and Nam, K.W., Challenges and possibilities for aqueous battery systems. *Communications Materials*, 4(1): 37, 2023.

[136] Zhang, Y.C., Ji, X.Y., Xie, C.D., Yang, R., Zhang, F. and Tang, Y.B., Aqueous Secondary Batteries: Status and Challenges. *Energy Storage Materials*: 104186, 2025.

[137] Yi, J. and Xia, Y., Advanced aqueous batteries: Status and challenges. *MRS Energy & Sustainability*, 9(2): 106-128, 2022.

[138] Liang, Y. and Yao, Y., Designing modern aqueous batteries. *Nature Reviews Materials*, 8(2):109-122, 2023.

[139] Insinna, T., Bassey, E.N., Märker, K., Collauto, A., Barra, A.L. and Grey, C.P., Graphite anodes for Li-ion batteries: an electron paramagnetic resonance investigation. *Chemistry of Materials*, 35(14): 5497-5511, 2023.

[140] Gao, X., Wu, H., Su, C., Lu, C., Dai, Y., Zhao, S., Hu, X., Zhao, F., Zhang, W., Parkin, I.P. and Carmalt, C.J., Recent advances in carbon-based nanomaterials for multivalent-ion hybrid capacitors: a review. *Energy & Environmental Science*, 16(4): 1364-1383, 2023.

[141] Deng, L., Wei, T., Liu, J., Zhan, L., Chen, W. and Cao, J., Recent developments of carbon-based anode materials for flexible lithium-ion batteries. *Crystals*, 12(9): 1279, 2022.

[142] Geim, A.K. and Novoselov, K.S., The rise of graphene. *Nature materials*, 6(3): 183-191, 2007.

[143] Das, S.K., Graphene: A cathode material of choice for aluminum-ion batteries. *Angewandte Chemie International Edition*, 57(51):16606-16617, 2018.

[144] Lobato-Peralta, D.R., Okoye, P.U. and Alegre, C., A review on carbon materials for electrochemical energy storage applications: State of the art, implementation, and synergy with metallic compounds for supercapacitor and battery electrodes. *Journal of Power Sources*, 617: 235140, 2024.

[145] Iqbal, S., Khatoon, H., Pandit, A.H. and Ahmad, S., Recent development of carbon-based materials for energy storage devices. *Materials Science for Energy Technologies*, 2(3): 417-428, 2019.

[146] Zhu, Y.E., Yang, L., Sheng, J., Chen, Y., Gu, H., Wei, J. and Zhou, Z., Fast sodium storage in TiO_2@ CNT@ C nanorods for high-performance Na-ion capacitors. *Advanced Energy Materials*, 7(22): 1701222, 2017.

[147] Han, M.C., Zhang, J.H., Li, Y.M., Zhu, Y.R. and Yi, T.F., Li5Cr7Ti6O25/multiwalled carbon nanotubes composites with fast charge-discharge performance as negative electrode materials for lithium-ion batteries. *Journal of the Electrochemical Society*, *166*(4): A626, 2019.

[148] Xu, K., Wang, L., Xu, X., Dou, S.X., Hao, W. and Du, Y., Two-dimensional bismuth-based layered materials for energy-related applications. *Energy Storage Materials*, 19: 446-463, 2019.

[149] Wang, A., Hong, W., Yang, L., Tian, Y., Qiu, X., Zou, G., Hou, H. and Ji, X., Bi-Based electrode materials for alkali metal-ion batteries. *Small*, 16(48): 2004022, 2020.

[150] Sun, J., Li, M., Oh, J.A.S., Zeng, K. and Lu, L., Recent advances of bismuth-based anode materials for sodium-ion batteries. *Materials Technology*, 33(8): 563-573, 2018.

[151] Finke, A., Poizot, P., Guéry, C., Dupont, L., Taberna, P.L., Simon, P. and Tarascon, J.M., Electrochemical method for direct deposition of nanometric bismuth and its electrochemical properties vs Li. *Electrochemical and solid-state letters*, 11(3): E5, 2007.

[152] Omori, Y., Honma, T. and Komatsu, T., Formation of bismuth metal in bismuth borate glass by reductive heat treatment and its electrochemical property as anode in

lithium-ion battery. *Journal of the Ceramic Society of Japan*, *126*(10): 820-825, 2018.

[153] Wang, C., Wang, L., Li, F., Cheng, F. and Chen, J., Bulk bismuth as a high-capacity and ultralong cycle-life anode for sodium-ion batteries by coupling with glyme-based electrolytes. *Advanced Materials*, 29(35): 1702212, 2017.

[154] Finke, A., Poizot, P., Guéry, C., Dupont, L., Taberna, P.L., Simon, P. and Tarascon, J.M., Electrochemical method for direct deposition of nanometric bismuth and its electrochemical properties vs Li. *Electrochemical and solid-state letters*, 11(3): E5, 2007.

[155] Ellis, L.D., Wilkes, B.N., Hatchard, T.D. and Obrovac, M.N., In situ XRD study of silicon, lead and bismuth negative electrodes in nonaqueous sodium cells. *Journal of The Electrochemical Society*, 161(3): A416, 2014.

[156] Su, D., Dou, S. and Wang, G., Bismuth: A new anode for the Na-ion battery. *Nano Energy*, 12: 88-95, 2015.

[157] Liu, S., Feng, J., Bian, X., Liu, J. and Xu, H., Advanced arrayed bismuth nanorod bundle anode for sodium-ion batteries. *Journal of Materials Chemistry A*, 4(26): 10098-10104, 2016.

[158] Wang, C., Wang, L., Li, F., Cheng, F. and Chen, J., Bulk bismuth as a high-capacity and ultralong cycle-life anode for sodium-ion batteries by coupling with glyme-based electrolytes. *Advanced Materials*, 29(35): 1702212, 2017.

[159] Gao, H., Ma, W., Yang, W., Wang, J., Niu, J., Luo, F., Peng, Z. and Zhang, Z., Sodium storage mechanisms of bismuth in sodium ion batteries: An operando X-ray diffraction study. *Journal of Power Sources*, 379: 1-9, 2018.

[160] Lu, C., Li, Z., Yu, L., Zhang, L., Xia, Z., Jiang, T., Yin, W., Dou, S., Liu, Z. and Sun, J., Nanostructured Bi 2 S 3 encapsulated within three-dimensional N-doped graphene as active and flexible anodes for sodium-ion batteries. *Nano Research*, *11*: 4614-4626, 2018.

[161] Sun, W., Rui, X., Zhang, D., Jiang, Y., Sun, Z., Liu, H. and Dou, S., Bismuth sulfide: A high-capacity anode for sodium-ion batteries. *Journal of Power Sources*, 309: 135-140, 2016.

[162] Fiordiponti, P., Pistoia, G. and Temperoni, C., Behavior of Bi2 O 3 as a cathode for lithium cells. *Journal of The Electrochemical Society*, 125(1): 14, 1978.

[163] Liu, T., Zhao, Y., Gao, L. and Ni, J., Engineering Bi_2O_3-Bi_2S_3 heterostructure for superior lithium storage. *Scientific reports*, 5(1): 9307, 2015.

[164] Zhang, J., Lu, X., Shi, X., Liu, H., Zhang, L. and Shi, X., Large-scale synthesis of BiOCl@ C composite as an anode material for lithium-ion batteries. *Inorganic Chemistry Communications*, 144: 109854, 2022.

[165] Guan, H., Dong, Y., Kang, X., Han, Y., Cheng, Z., Han, L., Xie, L., Chen, W. and Zhang, J., Extraordinary electrochemical performance of lithium–sulfur battery with 2D ultrathin BiOBr/rGO sheet as an efficient sulfur host. *Journal of Colloid and Interface Science*, 626: 374-383, 2022.

[166] Wang, D., Du, G., Wang, Y., Fan, Y., Han, D., Su, Q., Ding, S., Zhao, W. and Xu, B., BiOI nanosheets-wrapped carbon fibers as efficient electrocatalyst for bidirectional polysulfide conversion in Li–S batteries. *Chemical Engineering Journal*, 430: 133015, 2022.

[167] Fang, D., Cui, M., Bao, R., Yi, J. and Luo, Z., In-situ coating polypyrrole on charged BiVO4 nanowire arrays to improve lithium-ion storage properties. *Solid State Ionics*, 346: 115222, 2020.

[168] Durai, L., Moorthy, B., Thomas, C.I., Kim, D.K. and Bharathi, K.K., Electrochemical properties of $BiFeO_3$ nanoparticles: anode material for sodium-ion battery application. *Materials Science in Semiconductor Processing*, 68: 165-171, 2017.

[169] Nandi, S. and Das, S.K., An electrochemical study on bismuth oxide (Bi_2O_3) as an electrode material for rechargeable aqueous aluminum-ion battery. *Solid State Ionics*, 347: 115228, 2020.

[170] Nandi, S. and Das, S.K., Exploring the electrochemical activity of bismuth oxychloride for rechargeable aqueous aluminium–metal battery and a method for enhanced performance. *Bulletin of Materials Science*, 44(3): 234, 2021.

[171] Xie, J., Zhang, H., Liu, Q., Liu, X. and Lu, X., Recent progress of molybdenum-based materials in aqueous rechargeable batteries. *Materials Today Advances*, 8: 100100, 2020.

[172] Ruan, Q., Qian, Y., Xue, M., Chen, L. and Zhang, Q., Emerging two-dimensional Mo-based materials for rechargeable metal-ion batteries: Advances and perspectives. *Journal of Energy Chemistry*, 89: 487-518, 2024.

[173] Hu, X., Zhang, W., Liu, X., Mei, Y. and Huang, Y., Nanostructured Mo-based electrode materials for electrochemical energy storage. *Chemical Society Reviews*, 44(8): 2376-2404, 2015.

[174] Li, Z., Niu, B., Liu, J., Li, J. and Kang, F., Rechargeable aluminum-ion battery based on MoS_2 microsphere cathode. *ACS applied materials & interfaces*, 10(11): 9451-9459, 2018.

[175] Yang, W., Lu, H., Cao, Y., Xu, B., Deng, Y. and Cai, W., Flexible free-standing MoS_2/carbon nanofibers composite cathode for rechargeable aluminum-ion batteries. *ACS Sustainable Chemistry & Engineering*, *7*(5): 4861-4867, 2019.

[176] Tan, B., Han, S., Luo, W., Chao, Z., Fan, J. and Wang, M., of RGO-supported layered MoS_2 with enhanced electrochemical performance for aluminum ion batteries. *Journal of Alloys and Compounds*, 841: 155732, 2020.

[177] Tan, B., Lu, T., Luo, W., Chao, Z., Dong, R. and Fan, J., 2021. A novel MoS_2-MXene composite cathode for aluminum-ion batteries. *Energy & Fuels*, 35(15): 12666-12670.

[178] Malik, R., Joshi, N. and Tomer, V.K., Advances in the designs and mechanisms of MoO_3 nanostructures for gas sensors: A holistic review. *Materials Advances*, 2(13): 4190-4227, 2021.

[179] Avani, A.V. and Anila, E.I., Recent advances of MoO_3 based materials in energy catalysis: Applications in hydrogen evolution and oxygen evolution reactions. *International Journal of Hydrogen Energy*, 47(47): 20475-20493, 2022.

[180] Wang, C., Zhao, S., Song, X., Wang, N., Peng, H., Su, J., Zeng, S., Xu, X. and Yang, J., Suppressed dissolution and enhanced desolvation in core–shell MoO_3@ TiO_2 nanorods as a high-rate and long-life anode material for proton batteries. *Advanced Energy Materials*, 12(19): 2200157, 2022.

[181] Choi, S.H. and Kang, Y.C., Crumpled Graphene–Molybdenum Oxide Composite Powders: Preparation and Application in Lithium-Ion Batteries. *Chem SusChem*, *7*(2): 523-528, 2014.

[182] Wang, Z., Madhavi, S. and Lou, X.W., Ultralong α-MoO_3 nanobelts: synthesis and effect of binder choice on their lithium storage properties. *The Journal of Physical Chemistry C*, 116(23): 12508-12513, 2012.

[183] Hassan, M.F., Guo, Z.P., Chen, Z. and Liu, H.K., Carbon-coated MoO3 nanobelts as anode materials for lithium-ion batteries. *Journal of Power Sources*, 195(8): 2372-2376, 2010.

[184] Lee, S.H., Kim, Y.H., Parilla, P.A., Whitney, E., Gillaspie, D.T., Jones, K.M., Mahan, A.H., Dillon, A.C., Deshpande, R. and Zhang, S., Reversible lithium-ion

insertion in molybdenum oxide nanoparticles. *Advanced Materials (Weinheim)*, *20*: 2008.

[185] Lahan, H. and Das, S.K., Graphene and diglyme assisted improved Al^{3+} ion storage in MoO_3 nanorod: steps for high-performance aqueous aluminum-ion battery. *Ionics*, 25: 3493-3498, 2019.

[186] He, X., Zhang, H., Zhao, X., Zhang, P., Chen, M., Zheng, Z., Han, Z., Zhu, T., Tong, Y. and Lu, X., Stabilized molybdenum trioxide nanowires as novel ultrahigh-capacity cathode for rechargeable zinc ion battery. *Advanced Science*, 6(14): 1900151, 2019.

[187] Liu, Y., Wang, J., Zeng, Y., Liu, J., Liu, X. and Lu, X., Interfacial engineering coupled valence tuning of MoO3 cathode for high-capacity and high-rate fiber-shaped zinc-ion batteries. *Small*, 16(11): 1907458, 2020.