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Review

Metal-Ion Batteries: Achievements, Challenges, and Prospects

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Abstract: A new type of battery known as metal-ion batteries promises better performance than existing batteries. In terms of energy storage, they could prove useful and eliminate some of the problems existing batteries face. This review aims to help academics and industry work together better. It will propose ways to measure the performance of metal-ion batteries using important factors such as capacity, convertibility, Coulombic efficiency, and electrolyte consumption. With the development of technology, a series of metal ion-based batteries are expected to hit the market. This review presents the latest innovative research findings on the fabrication of metal-ion batteries with new techniques.

Keywords: metal-ion batteries; Ca batteries; Mg batteries; Zn batteries; Na batteries

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1. Introduction

The use of lithium-ion batteries has been increasing over the past few years. It is believed that the market value of lithium-ion batteries will grow from USD 30 billion in 2017 to USD 100 billion in 2025, although their use in large-scale operations is limited by certain issues. Li-ion batteries can be very expensive to make. These batteries are about 40% more expensive to make than nickel metal hydride batteries. In cases of overheating or increased power supply, devices may become damaged faster. Concerns about the safety of Li-ion batteries are common among the public [1–3].

A special type of battery called Li-ion batteries can explode when it becomes too hot or overcharged. This happens because of the gases made by the liquid used in the process. Transporting large Li-ion batteries can cause difficulties. Batteries made from lithium ions age and do not work well after 500 to 1000 uses. There are some issues with making better batteries using Li-ion technology. Though lithium is a valuable resource, it is difficult to find. Insufficient lithium can lead to increased monetary and ecological dilemmas. The profitability of obtaining minerals with low lithium content will increase if the cost of lithium rises. Although it may be easier and more cost-effective to dispose of objects rather than recycle them, this practice has adverse consequences on the environment, such as heightened energy consumption and waste during the creation of fresh products [4–6].

Zinc, magnesium, calcium, and sodium are types of batteries that can be charged and used to store energy. They are popular choices for new energy storage devices. Zn-ion batteries are safe as water is used as the electrolyte. Zn-ion batteries can be made from materials that are easy to find. Zinc batteries are cheaper and last longer than lithium-ion batteries.

The use of Mg ion-based rechargeable batteries is increasingly common as a novel energy storage solution. Mg is cheap and abundant on Earth, and can store a substantial amount of energy. Large-scale endeavors can greatly benefit from it. Using Mg as a cathode

is affordable and good for the environment because it does not produce any harmful substances [7].

Ca-ion batteries are another option for new high-energy storage devices. Calcium is an element commonly found in soil. It is not harmful and has a certain electrical charge. In simpler terms, Ca^{2+} ions move more easily in liquids because they are less affected by their surroundings than Mg^{2+} and Al^{3+} ions [8]. Simply put, switching from using lithium to using zinc, magnesium, or calcium can help save energy and money, and is better for the environment than using lithium metal. Na-ion batteries are a good option for large projects where cost is more important than how much energy the battery holds. This is because batteries made with sodium cannot hold as much energy as batteries made with lithium [9,10]. A new concept of interest to researchers is Na-ion due to the low cost, and abundance of mineral raw materials.

2. Multivalent Batteries

The application and commercial use of multivalent batteries (Ca, Zn, Mg) can attract attention due to their facile process, nontoxicity, and safety. Improved composite electrode materials and tuning electrolyte systems can enhance capacity, cycle life, and energy density. Thus, they are critical for the commercialization of multivalent batteries. They offer a safer, more sustainable, and low-capacity fading alternative for the future of electric vehicles.

2.1. Ca-Ion Batteries

Compared with bi-charged magnesium, multi-charged calcium is relatively weak in polarization. This means it can react faster than magnesium. If Ca^{2+} is present, it is easy for M^{x+} ions to pass through the electrolyte layer because the energy barrier is low. In simpler terms, M sticks easily to the electrode. The liquid, salt, how much electrolyte there is, temperature, and what it interacts with can all affect how well the process works. These all affect how well something will adhere to or interact with another substance. Other factors include how hot it is, what the surface is made of, and the mixtures of fluids and minerals used. We will see how the M^{x+} ions move through the electrolyte and whether they stick together (ion coupling) [11,12].

A few factors to consider are how difficult something is to dissolve, what is in the layer between the electrodes (and how it can conduct electricity), and how difficult it is for new particles to form. These fundamental issues should be properly addressed. To make good calcium metal anodes, the electrolyte must have Ca^{2+} ions, and the addition and subtraction of calcium metal multiple times must be feasible. To adhere metal to something, scientists use a special layer on top of an electrode. The plating/stripping process of calcium in electrolyte could be hindered owing to highly sluggish kinetics in pure Ca-SEI interphase. Reduced charge transfer resistance, enhanced solvation/desolvation kinetics, and significantly lowered overpotentials in deposition and dissolution processes result in a slow diffusion energy barrier.

Ponrouch and his team investigated substances that might be good electrolytes. They should be stable, not too thick, and break up salts easily. They looked at different types of liquids that do not contain protons (called polar aprotic solvents), such as alkyl carbonates, to see if they could be used as electrolytes to make better batteries for electric cars that use calcium. These liquids can dissolve salts very effectively, and also, because they are not thick (low viscosity), they help electricity flow better. Some of their notable features include their capacity to withstand high temperatures and electrical currents without any signs of deterioration or malfunction [11,12].

Ca batteries are similar to Li-ion batteries on the positive electrode. As the electric charge is discharged, it shifts in a certain direction. The ion carrying the (Ca^{2+}) charge moves. Electricity flows in an electrolyte from the positive end to the negative end. Electrons traverse a circuit operating outside of a mechanism (Figure 1).

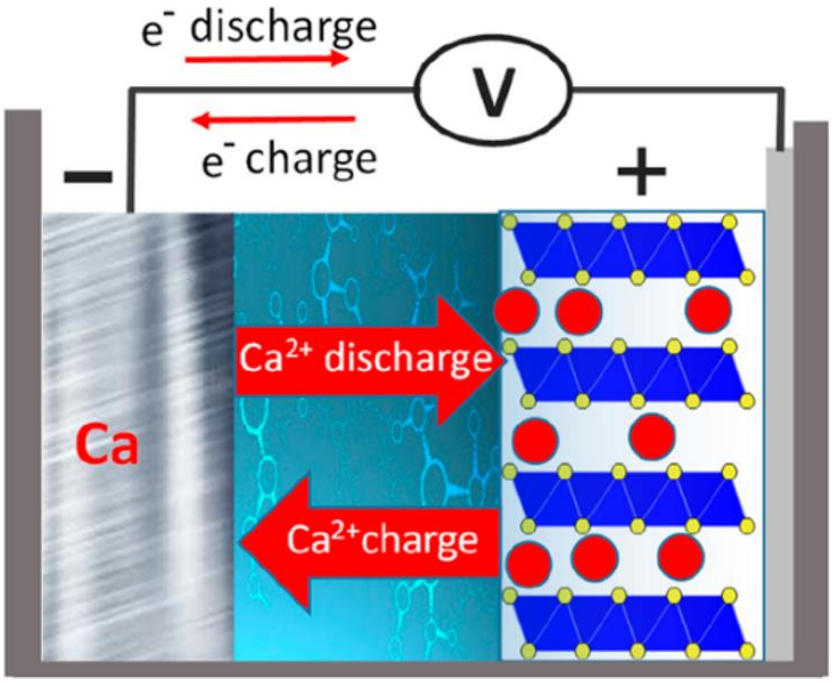

Figure 1. Schematic of a Ca battery using a Ca metal anode and an intercalation cathode. Reproduced with permission from ref. [13].

2.2. Zn-Ion Batteries

Zn-ion batteries are currently the focus of attention of many scientists. Zinc metal and a special liquid containing zinc are inside these batteries. Also, the battery has a part that traps zinc ions. This is because there are numerous types of liquids that can conduct electric current, including those with and without water. Also, zinc can conduct electricity very well when mixed with water, making it a good choice for batteries. Using zinc batteries is also safer and less harmful to the environment [14,15].

To sell Zn-ion batteries, we need to focus on developing better materials for the part that attracts electrons (the cathode), the liquid that carries the charge (the electrolyte), and the part that provides the electrons (the zinc anode). Experts have looked at different substances to use as cathodes in batteries that use zinc ions. Some of the substances they work with include manganese, vanadium, Prussian blue analog, spinel-structure oxide and organic materials [16,17].

Manganese dioxide can have different shapes, which are called α-MnO_2, β-MnO_2, γ-MnO_2, and δ-MnO_2. Some scientists are trying to make MnO_2 more conductive and longer-lasting. In our opinion, when we look at MnO_2-based cathodes, we think that the best materials to be used as cathodes are α-MnO_2 and γ-MnO_2. α-, β-, and γ-MnO_2 polymorphs have recently been investigated. α and γ-MnO_2 have a larger tunnel size in comparison with β- MnO_2, *resulting in* superiority in both cycling and rate performance. β-MnO_2 exhibits a high reversible capacity and stable cyclability.

A material called α-MnO_2 has a special structure and is being studied as a material for use in batteries using zinc [18,19]. The material called γ-MnO_2 is very good for adding and removing Zn^{2+} because it has many tunnels that are not arranged in any particular order. Vanadium oxide can be used in batteries instead of other materials to store energy. Vanadium-based compounds, especially vanadium-based oxides, are frequently used to store zinc due to their low cost, easy availability, and ability to exist in different oxidation states ranging from V^{2+} to V^{5+}. A significant concern with vanadium is that if the zinc is added or removed too quickly, it can quickly deteriorate the way it is constructed. The ability of vanadium-based electrodes to carry electricity needs to be improved so that it becomes easier to store and remove electrical charge. Also, electrode design with more exposed active areas and a combination of conductive materials has been proven to work

better. For batteries to work better, the energy transfer ability of vanadium electrodes must be improved. Researchers suggest using substances called Prussian blue analogue and spinel-structure oxide in ZIBs. These substances have structures similar to other chemicals ($ZnMn_2O_4$, $ZnAlxCo_{2-x}O_4$, and $ZnNi_xMnxCo_{2-2x}O_4$) and improve the way ZIBs work by helping Zn^{2+} move more easily. Cathode-forming organic materials can create good places to store zinc ions [19]. Scientists have made a new type of battery part called an organic cathode, which is very promising. It uses a type of molecule called quinone to store a substance called Zn^{2+}.

Quinone molecules have special parts that can hold Zn^{2+} like a handshake. Protons can easily move through the attached system of amino and carbonyl groups, thanks to a special bonding process called the Grotthuss mechanism. Therefore, proton insertion enhances kinetics and is favored for energy storage.

Batteries that use Zn ions have several different types of liquids and gels inside that help them work. These are called electrolytes. Some types of electrolytes are made from water, while others are made from special liquids or gels. There are different types of electrolytes, such as ionic, organic, and solid ones. The type of liquid used in Zn batteries affects how well they work and how much energy they can hold. Choosing something called an "electrolyte system" is now very important [20,21]. Depending on the types of cathode materials and how they store energy, we need to make a connection between the electrolyte system and how the battery works together. If a system uses magnesium cathodes, it must contain water for important reactions to occur.

In real life, the cost of an electrolyte system cannot be changed. The "water in salt" electrolyte is not good for vanadium-based cathodes, although it can conduct electricity well and has a wide stability range. It is important to consider how much liquid and liquid electrolyte to use for Zn-ion batteries to work better and be easier to use. To make flexible batteries using zinc, we need to make sure the gel and semi-solid materials have the right qualities. These include being strong, bendable, and stable at different temperatures and not reacting with chemicals. We also need to make sure that they work well when electricity flows through them. To make better electrolytes, we need to examine how they work when used in a battery [21,22].

Our aim is to provide high energy storage capacity and extended durability and maintain environmental friendliness at an affordable price. The future requires a deeper exploration of these concepts.

A Zn anode is oxidized to provide Zn^{2+} upon discharge, while a reduction reaction occurs on the cathode. The cathode materials vary from transition metal-based oxides, MXsenes, and organic compounds to O_2 (Figure 2).

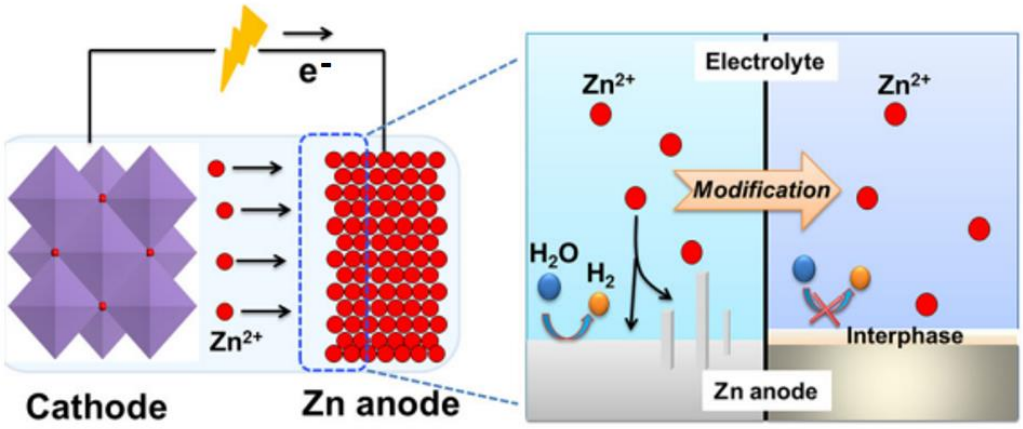

Figure 2. Schematic representation of modification strategies for rechargeable Zn batteries. Reproduced with permission from ref. [22].

2.3. Mg-Ion Batteries

Mg-ion batteries are not yet fully developed, but they could become a better way to store energy for electric cars as they are safer and more sustainable and can hold more energy. Cathodes are important parts of Mg-ion batteries. These batteries can be divided into two types: intercalation and conversion [23]. Cathodes using intercalation can stay the same throughout the reaction, which helps them last a long time without breaking down. There are three types of materials called intercalation cathodes: layered materials, Chevrel phase materials, and polyanionic compounds. Researchers are interested in Chevrel phase and layered materials, but there are some problems, such as the slow movement of magnesium ions, that make them difficult to use in real life [24,25].

Polyanionic cathodes are strong and have a lot of voltage, but they do not conduct electricity very well. Experts have discovered that conversion cathodes are better at storing energy than intercalation-type cathodes. The most commonly used cathodes for conversion are sulfides and organics. To have a good battery, we need to consider three things: it must store a lot of energy, it must have a strong electrical charge, and it must be able to be recharged many times. Sulfur cathodes are the best material for cathodes in batteries that use magnesium ions. This is because they have a very good energy storage capacity and can last a long time without wearing out [24–26].

Researchers are considering using inexpensive organic materials as cathodes, as they are easy to work with chemically. A quinone-containing mixture may work similarly to sulfide cathodes. The appearance of the quinones can be changed using new materials and a special design. This can lead to even better results.

The contents of a Mg-ion battery need to be special. They should not damage the interior of the battery, should allow easy movement of electrical ions, should not evaporate quickly, should not be dangerous, and should be able to withstand high temperatures. There are two types of liquids, called liquid- and solid-state electrolytes, that can be used in batteries that use magnesium. There are three types of liquid electrolytes: Grignard, boron, and $(HMDS)_2$ Mg. Grignard electrolytes can ensure that a layer that prevents magnesium from moving is not formed, allowing the magnesium to move back and forth easily [26,27].

Boron chemicals can be useful to move ions back and forth, and they do not harm substances like chlorine. An $HMDS_2Mg$ electrolyte can be used with sulfide cathodes as a good option. It is a type of electrolyte that is unlikely to react with other substances and can work well with cathodes. The electrolyte can also withstand a high level of energy input. Adding lithium salt (LiTFSI) to $(HMDS)_2Mg$ can make batteries better because it helps increase their capacity, energy density, and lifespan when they use a magnesium electrode and a sulfide cathode. This type of electrolyte is expensive as it has special elements called electrolytes [27,28].

Recently, scientists have been investigating solid-state electrolytes more closely because they are safe, strong, powerful, and work well in different situations with different amounts of power. There are three different types of composites: inorganic, organic, and organic–inorganic. Some types of solid electrolytes do not conduct electricity very well, but others do. They have a good balance of conductivity, polarization, and stability over time. These better ones are made from organic materials. A mix of natural and artificial materials with small parts and special fluids can help solve the problems mentioned earlier. This special liquid can work better and last longer when used in batteries. It has been noted that solid electrolytes are safer and less corrosive, but they still have compatibility issues.

Magnesium ions are moved between a negative anode and a positive cathode made of a metal oxide material. This allows electrons to be transferred around an external circuit. (Figure 3).

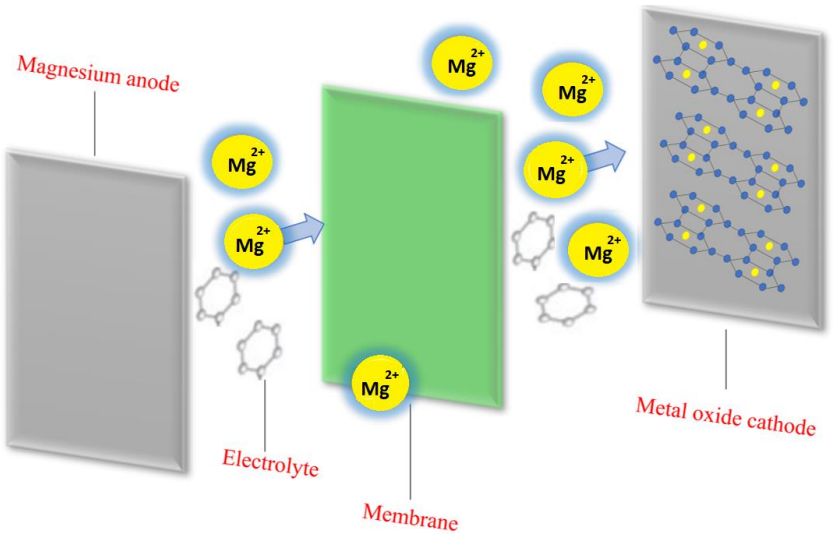

Figure 3. Schematic representation of modification strategies for rechargeable Mg batteries.

3. Monovalent Batteries

Recent years have seen an increase in high-quality articles and research on Na-ion batteries. This area may undergo significant changes as a result.

3.1. Na-Ion Batteries

Sodium-ion batteries are considered as an alternative to lithium-ion batteries. They are similar in that they have the same chemistry as lithium, a common metal. Using sodium batteries can be cheaper and better for the environment. Sodium is difficult to use because it is larger and heavier than lithium [29]. To make a good sodium-ion battery, we need to use the right materials for the anode and cathode. This is important if we want to sell the battery commercially. This means that scientists need to find and create materials for batteries that can hold a lot of sodium ions to store large amounts of energy [30].

While there are numerous alternatives for sodium-based positive electrodes, hard carbon has emerged as the most suitable negative electrode. Since two types of reactions (insertion and conversion) occur at the same low energy level, there are not many options for transition metal oxides. Addition reactions work better with the 3D metals used initially [31]. Scientists have discovered that $Na_2Ti_3O_7$ is a good substance to use for sodium batteries at low cost, although they previously thought $NaxVO_2$ was the best [32]. It can exchange 2 Na (sodium) ions per unit and has a back-and-forth process. It can hold 200 milliamp hours of electricity per gram and operates at 0.3 volts. The sodium ions become neutral sodium atoms [33]. The layer formed between the electrode and the electrolyte (SEI) is not strong enough to use sodium in batteries. We need to study further to find out how the components change during redox. We also need to understand what the SEI is made of and how it is formed [34].

There are different types of materials that can be used in sodium-powered batteries. Alloy materials are an example. The reaction mechanism is like how substances react in lithium mixtures. When mixed with elements from IV and V groups such as Na, Sn, Ge, P, and Sb, they can hold more energy than carbon materials. The maximum energy capacity (in theoretical calculations) for these mixtures is 847, 1108, 2595, and 660 mAh g^{-1}, respectively [35,36].

Although sodium-ion batteries can store a lot of energy, they have some problems that make them difficult to use, such as being too large and breaking apart when charged and discharged [37].

Carbon and metallic materials are the most effective solutions for preventing excessive bending or expansion of an object. Carbon-based materials have often been used in past studies as they are strong and conduct electricity well, and are good for storage. Fan

et al. used a mixture of materials called amorphous-SnO_2/graphene airgel to make parts of a rechargeable battery, called anodes. After 100 cycles, one type of electrode with no definite shape was able to hold a good amount of discharge capacity, about 380.2 mAh g^{-1}. This was about three times more than a similar type of electrode with a specific crystal structure [38] produced by Ramakrishnan and colleagues. As a result of combining the two substances, a new compound Sb_2O_4/graphene, was developed. It can store a lot of energy and still works well for a long time. We tested it many times and it continued to work well [39]. Electrospinning of Sb-C nanofibers were investigated by Lin's group. The Sb-C nanofiber electrode was tested and found to be able to charge and discharge faster than other electrodes (337 mA h g^{-1} at 5 °C). It also showed a greater energy storage ability (631 mA h g^{-1}) and can last for a long time without losing capacity (90% capacity retention after 400 cycles) [40].

Liu and his team investigated a small piece of material called Ge that was made into even smaller pieces and added to special fibers, helping them to withstand size changes during charging and discharging. There are gaps in the carbon structure that can help Ge nanoparticles grow and allow Na ions to flow easily [41]. Pan and his team examined how well GeO_2/rGO was able to store sodium. The anode can hold 330 milliamp-hours of energy per gram when slowly charged and discharged. It can also last for more than 600 cycles when charged and discharged quickly [42].

Ying et al. made a material called Sn/N-doped carbon microlattice composites (Sn/NMCs). Carbon matrices help stabilize the bulk of materials, make energy storage processes more efficient, and provide fast paths for electrons and sodium ions to move around. The material worked well and initially had sufficient strength [43]. It retained the same power level even after 300 uses. Chen and his team made tiny particles called Sn nanoparticles and put them inside tiny cages made of carbon called graphite porous carbon nanolatches. Their study describes using a special method to carry out a process called CVD. They use a technique that helps make CVD where it is needed. The material had enough room to store more energy and could be used for a long time without losing its effectiveness, even when used at high speeds. It can store energy up to 828 mA h g^{-1} [44].

The use of phosphorus in sodium storage devices causes size increase, slow response speed, and poor conductivity of electricity [45].

Sun et al. made tiny particles about 10 nanometers across and placed them in a 3D carbon frame. Small phosphorus particles can remove the pressure without breaking, facilitate the movement of electricity, and adhere well to the carbon material [46]. They can store a certain amount of energy and release it as needed. Liu and his team made a small porous material called NPRP and put it on a conductive material called RGO. This can be used as a battery component called the anode. This can provide power to objects very quickly and can maintain it for a long time without wearing out. It can run for more than 1500 cycles and can hold a lot of energy each time it runs [47]. Yao and his team created a new type of carbon sphere with voids inside. 135 is a type of P/C composite material. This mixture expanded a bit and remained stable after many uses. After 1000 cycles, a large portion of its original capacity was still left [48].

In 2004, Geim of the University of Manchester discovered how graphene is made, a new type of material that is only two-dimensional. This discovery is very important [49]. Recently, scientists have been working on special chemicals made of metal and sulfur, flat structures made of metal and organic materials, and patterns formed by metal atoms. "Gogotsi et al." refers to a group of researchers led by Gogotsi. In 2011, scientists made a material called MXene using a chemical called hydrofluoric acid. MXene is very strong, does not rust easily, and can conduct electricity and heat well. Other uses for this material are to store energy, help chemical reactions happen faster, convert methanol to another substance, create hydrogen, and increase how much energy can be stored and used quickly [50]. MXene is a material that can be used to form substances such as oxides, sulfides, and nitrites. It has similarly superior discharge capacity, long cycle life, and high energy density. "MXene derivatives have special electrical properties because they can strongly absorb Na

and K and have large gaps between their layers." There are reports that different materials are used on the positive end of batteries. These materials are usually in layers or not in layers. Wu and his team created a material by combining MoS_2 and $Ti_3C_2T_x$. They created a gap in the layer that helps the ions reach the MXenes better, making them stronger. The material had a better initial ability to hold energy at 67% after 100 uses and was able to store 250.9 mAh g^{-1}. Du et al.'s research found that mixing $Ti_3C_2T_x$ and MoS_2 nanolayers produces a battery with strong performance. It maintained high capacity for a long time, even after 70 cycles. Wu and his team made small structures by combining MXene and SnS_2 sheets [51]. The new material, named MXene@SnS_2, can store more energy than other similar materials. It can hold 322 mAh g^{-1} of energy after being charged and discharged 200 times. This is better than just using MXenes or other types of materials [52].

It is important to choose the most suitable electrolyte to increase sodium storage in batteries. In the last decade, individuals have made significant efforts to develop Na-ion batteries. Batteries have attracted great interest due to their versatile energy storage capabilities. According to the literature, aqueous substances with charged particles help batteries work better and stay powerful. Batteries that use Na ions in water can teach us a lot about how they work and what can be achieved with them in the future. They can be used for important things. However, we should pay attention to different problems such as side effects, mixing of the protons with the cathode materials, changing the pH of the electrolyte while charging or discharging, and corrosion of the cathode. These will affect not only the chemistry of water-based batteries, but also their ability to store energy and last longer [53].

The properties of MXenes, such as their high conductivity and layer spacing, make them a suitable material for batteries. Their surfaces are engineered for optimal performance and include multiple layers with distinct properties. Sodium-based MXenes create self-standing and flexible batteries [52–54].

Li compounds exhibit unusual rhythms due to the small size of Li^+ ions. Because of their strong bonds, lithium oxides, carbonates, and hydroxide can be difficult to dissolve in certain liquids. The use of sodium electrolyte facilitates the dissolution of surface materials. The addition of lithium electrolyte results in a more stable composition with a reinforced protective layer. Meanwhile, non-polymerized organic solid electrolyte interphase (SEI) components in Na electrolyte result in increased dissolution of the surface species. During charging, sodium ions are extracted from the cathode and moved toward the anode, while the electrons transfer through the external circuit. During discharging, the reverse process occurs (Figure 4).

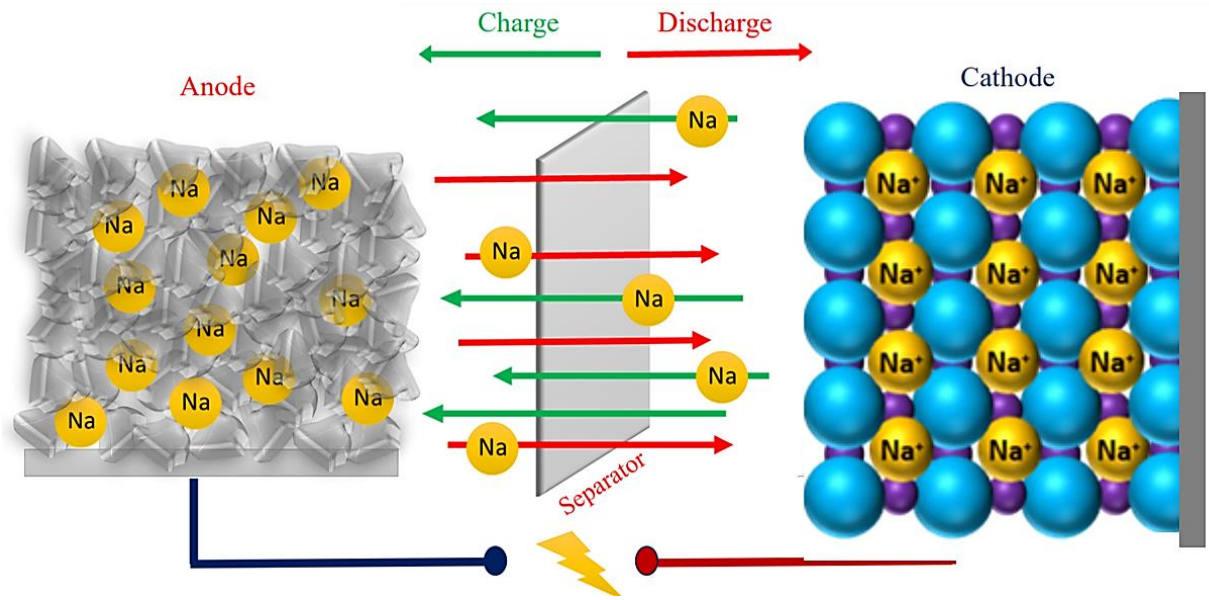

Figure 4. Schematic representation of modification strategies for rechargeable Na batteries.

3.2. K Ion Batteries

Potassium-ion batteries (K-ion), as another alternative for Na-ion batteries, have low electrical conductivity and a significant volume change, which restricts their electrochemical performance and commercial application. The practical design of cathodes and novel electrolytes need to be investigated for commercial application of K-ion batteries.

4. Summary and Conclusions

To make composite electrodes that can improve energy storage and stability during cycling, we need to study new nano materials and ways of making them. We can improve properties by making them the right shape, size, or structure.

By using methods such as surface engineering and adding other materials, we can improve how well anode materials work in metal-ion batteries. This is because these methods help solve problems with how quickly materials react and conduct electricity. Also, a battery's initial ability to store and release energy can be improved by modifying the surfaces of its particles and creating an appropriate composition, structure, and shape.

Safety, environmental friendliness, low cost, and energy density need to be considered for commercial needs. Zn-ion batteries are safe, environmentally friendly, and low-cost, with high energy density. Mg-ion batteries are safe and low-cost, with high energy density and no dendrite formation. Ca-ion batteries have less polarization potential with high cell voltage. Na-ion batteries are more abundant, low-cost, and safe and do not easily produce dendrites. Overall, Zn-ion and Na-ion batteries could meet all demands for commercial needs [55,56].

We can discover and develop new materials for metal-ion batteries by studying experiments and using theories. This will help us understand how materials store ions and how their structure affects their performance.

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