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Entry

Metal-Ion Batteries

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Definition: Metal-ion batteries are systems for electrochemical energy conversion and storage with only one kind of ion shuttling between the negative and the positive electrode during discharge and charge. This concept also known as rocking-chair battery has been made highly popular with the lithium-ion battery as its most popular example. The principle can also be applied with other cations both mono- and multivalent. This might have implications and advantages in terms of increased safety, lower expenses, and utilizing materials, in particular metals, not being subject to resource limitations.

Keywords: metal-ion battery; rocking-chair battery; secondary battery; accumulator

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1. Introduction

In a secondary battery commonly employed for electrochemical energy conversion and storage commonly two electrodes and an electrolyte (solution) are employed with electrode reactions proceeding at both electrodes with more or less significant changes in the composition of the electrolyte (solution). Frequently constituents of the electrolyte solution are consumed or new ones are generated. The associated changes of properties of the electrolyte (solution) are mostly unwelcome because they might e.g., result in reduced ionic conductivity and increased internal resistance of the device. In addition, these changes require a certain minimum amount of electrolyte (solution) for the electrode reactions to proceed. These disadvantages are absent with the metal-ion battery. Because all known examples work with a common cation A^{n+} the electrode reactions can be written for the negative electrode during discharge as

$$A \rightarrow A^{n+} + e^{n-} \tag{1}$$

and for the positive electrode during discharge assuming a host material B capable of accommodating A or A^{n+} with associated valency changes in

$$B + A^{n+} + e^{n-} \rightarrow BA \tag{2}$$

Assuming a metal electrode as the negative one the principle is illustrated in Figure 1. For various reasons addressed for specific materials below a metal may not be suitable, instead a host material H is also employed as a negative electrode. This results in a modified electrode reaction of the negative electrode

$$H(A) \rightarrow H + A^{+} + e^{n-} \tag{3}$$

illustrated in Figure 2.

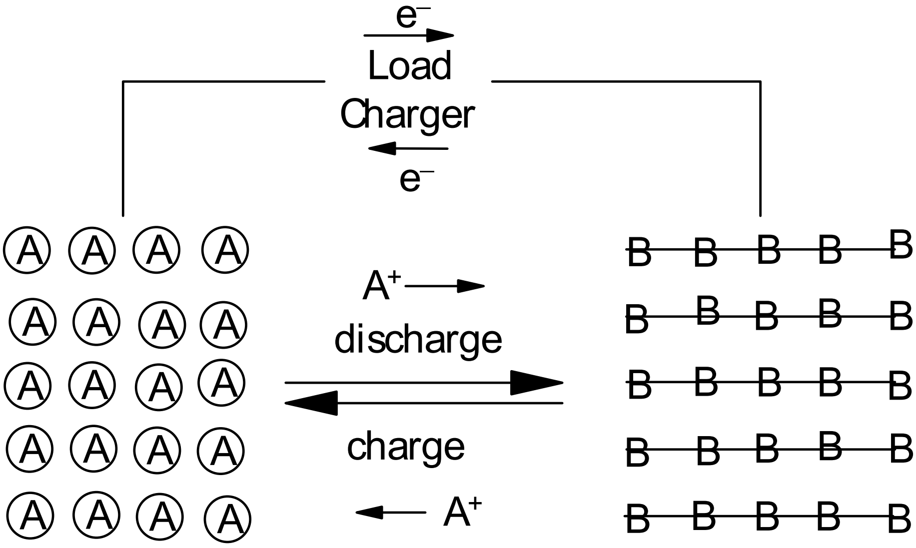

Figure 1. Principle of a rocking-chair battery, a positive intercalation-type electrode is assumed.

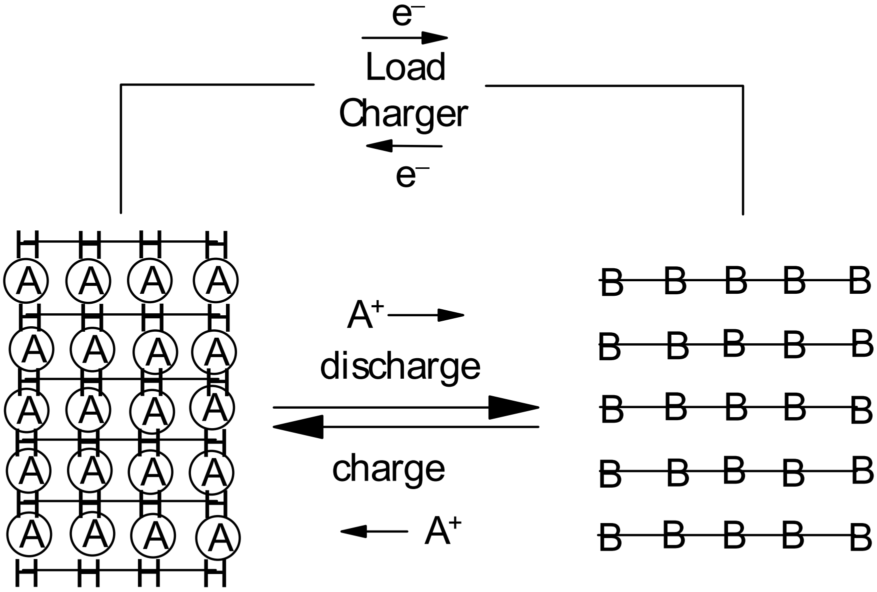

Figure 2. Principle of a rocking-chair battery, both negative (H) and positive (B) intercalation-type electrodes are assumed.

The obvious advantage of this concept results from the fact, that there are no net changes in the electrolyte composition; all associated negative effects of this are absent. Beyond this obvious advantage there is another benefit: only a minimum amount of electrolyte (solution) is needed, just enough to enable the shuttling of the respective ions. Thin layers of gelled electrolyte or solid electrolytes are conceivable; in the case of liquid electrolyte (solution) just the amount necessary to soak the separator and to fill the porous electrode materials is needed. Beyond the obvious cost and safety benefits the cells may have increased energy densities because of the decreased amounts of material basically not actively contributing to storage.

This concept has turned out to be highly successful with the omnipresent lithium-ion battery. There are nevertheless several limitations and drawbacks seriously limiting the further expansion of this system. Limited resources of both lithium as the active metal-ion as well as further ingredients of the positive electrode in particular may turn out to be serious confines. In addition the safety concerns associated with the behavior of lithium, its dendritic deposition especially at high charging currents, and storage capability limitations of several frequently employed and/or investigated materials are noteworthy. Thus research into transferring the basic benefits into systems with other cations A^{n+} has started.

2. State of the Art

Several metals/cations have been examined. Obvious criteria for selection are high availability, acceptably negative electrode potential of the metal, highly reversible metal dissolution and redeposition, competitive costs, and environmental compatibility. For evaluation from an electrochemical point of view it is insufficient to take just the electrode potential or another single property of a given material, this has resulted in rather misleading estimates and promises as pointed out in a review [1]. Because the energy density of a cell depends on both electrodes, their charge storage capabilities as well as their working electrode potentials a comparison taking as the other electrode in the present context (the positive electrode or cathode) either a high-potential material such as Mn_2O_4 spinel with moderate capacity or a high capacity material such as sulfur with a lower electrode potential [1].

In addition to monovalent cations/metals such as sodium and potassium attracting attention as obvious replacements of lithium di- and trivalent (multivalent) cations/metals have been considered. The obvious advantage—two or even three electrons are released during the discharge reaction of a single cation—does not necessarily translate into a more promising system. The electrode potentials of many examined metals are much less negative than those of the alkali elements. Accordingly lower energy densities, which take into account both electrode potentials and cell voltages in addition to charge storage capabilities, are frequently found. Table 1 provides an overview [2].

Table 1. Some characteristic data of potential candidate materials for metal-ion batteries [2].

Element	Atomic Mass	$E_{00,\,\mathrm{SHE}}$/V	Gravimetric Capacity/mAh·g^{-1}	Volumetric Capacity/mAh·cm^{-3}
Li	6.94	−3.040	3860	2061
Na	23.0	−2.713	1165	1129
K	39.1	−2.924	685	610
Mg	24.31	−2.356	2206	3834
Ca	40.08	−2.840	1337	2072
Zn	65.41	−0.763	820	5855
Al	26.98	−1.676	2980	8046

The data in Table 1 alone are of limited value only when estimating the competitiveness of a given material [1]. Although frequently energy and power densities have been discussed for a single electrode material (actually this does not make sense at all, there exists no battery with only one electrode) a more realistic comparison should be based on realistic electrode couples (i.e., cells), of course preferably using the same material for the positive electrode (as has been stressed many times before use of the terms anode and cathode is only confusing when discussing secondary batteries, it is thus strictly avoided in this text). Given the rather limited number of even distantly suitable materials selection is difficult; Mn_2O_4 and sulfur have been suggested [1].

All listed metals have standard potentials negative to the hydrogen electrode, thus at first glance aqueous electrolyte solutions generally attractive for numerous reasons are not applicable. This consideration based solely on thermodynamic constraints is incomplete. When taking into account kinetic aspects, in particular hydrogen overpotentials, the picture changes slightly. In case of zinc the overpotential is notable, thus there may be hope for a zinc-ion battery with an aqueous electrolyte solution becoming a storage option. The numerous advantages of water as a solvent for an electrolyte solution are closely connected to a major drawback: Its narrow window of electrochemical stability, i.e., the range of electrode potentials, which are combined into the voltage, wherein the electrolyte solution remains stable and is not decomposed, of about 1.23 V. Even when taking into account electrode overpotentials of both the negative electrode (see above) and the positive electrode (oxygen evolution is also kinetically slow at many materials) utilization of this seeming advantage and thus escaping a bit from a fundamental limitation comes at a further prize: most likely higher self-discharge [3,4].

Research and development in particular with monovalent cations started with the optimistic assumption, that concepts and materials well-established in lithium-ion battery technology could be transferred rather straightforwardly into sodium and potassium battery technology. Different cation sizes and associated different charge densities and associated changes in solvation and desolvation resulted rather early in frustrating results regarding e.g., poor performance data of graphite as a negative host material as well as many positive electrode materials mostly of the intercalation or insertion type. New materials or variants of the known ones taking into consideration said ionic differences and results of theoretical calculations are currently examined. Because of the significant differences between the mono-, di- and trivalent cations they are considered separately following.

2.1. Monovalent Cations

Until now, the most studied secondary batteries based on monovalent alkali metal ions are lithium-ion (LIBs), sodium-ion (SIBs) (most fortunately there is only one incident this battery has been called NIB), and potassium-ion (PIBs) batteries, respectively. Lithium-ion batteries working as power sources for portable, mobile, and wearable applications as well as in electric vehicles are dominating the current market of rechargeable batteries.

Lithium has a theoretical specific capacity of 3860 mAh·g^{-1} and a highly negative standard electrode potential (-3.040 V vs. SHE). The effective ion radius of Li^+ is around 0.76 Å; this is the smallest radius of all metal ions in metal-ion batteries. Because lithium cannot be safely plated from its ionic solution and in particular without dangerous dendrite formation graphite has been employed as host material (see Figure 2) wherein lithium can be intercalated at electrode potentials close to that of the lithium electrode [2]. However, apart from these advantages, the LIBs face serious drawbacks including high costs, insufficient safety, limited resources, and insufficient energy density. Options and challenges for beyond-lithium batteries have been collected elsewhere [5,6].

Hence, these unsolved problems motivated scientists to develop other non-lithium-ion batteries with high sustainability and performance beyond LIBs. Compared to the LIBs, the Na^+-ion and K^+-ion batteries possess the advantages of highly abundant and cheap raw materials. The lower Lewis acidity of sodium and potassium ions leads to smaller size of the solvated ions when compared with Li-ions. The lower desolvation energy will benefit ion diffusion and passage through the electrolyte/electrode interface. The relative atomic masses of Na and K are 23.0 and 39.1, respectively. According to Faraday's law

$$C_0 = \frac{n \cdot \mathrm{F}}{3.6 \cdot M_w} \tag{4}$$

where C_0 in mAh·g^{-1} represents the theoretical gravimetric capacity, n is the number of charge carriers, F is the Faraday constant (F = 96,485 C) and M_w is the molecular weight of the active material. The charge density of battery electrode materials largely depends on the relative atomic mass, so that both gravimetric and volumetric capacity of Na (1165 mAh·g^{-1}

and 1129 mAh·cm^{-3}) and K (685 mAh·g^{-1} and 610 mAh·cm^{-3}) are lower than that of Li. The effective ion radii of Na$^+$ (~1.02 Å) and K$^+$ (~1.38 Å) are remarkably larger than that of Li$^+$ (~0.76 Å), which can lead to sluggish diffusion and reaction kinetics. Therefore, it is a big challenge to find appropriate electrode materials with internal spaces large enough to host Na$^+$ and K$^+$. As of today, these disadvantages suggest SIBs and PIBs could be used in large scale stationary energy storage systems rather than in mobile battery systems. Progress in aqueous SIBs and PIBs has been reviewed [7].

Hard carbon materials as negative electrodes for sodium-ion batteries have been examined and compared with materials for lithium- and potassium-ion batteries [8]. Furthermore, general carbon-related reviews are available [9,10]. Materials and approaches towards sodium-ion batteries were examined in [11–13], in a further report presentation of sodium-ion battery electrode material-related information has been mixed for unknown reasons with some information on positive electrode materials for magnesium-ion batteries [14]. Sodium ion storage in titanates (apparently in the negative electrode) has been reviewed [15], further inorganic positive electrode materials have been discussed in [16], negative intercalation materials are treated in [17], and amorphous carbon materials have been the topic in [18]. Polymer electrolytes for sodium-ion batteries were the subject in [19], aqueous systems the topic in [20,21], non-aqueous systems in [22], and solid electrolytes in [23]. Advanced positive electrode materials have been briefly inspected [24]. Cobalt-free positive electrode materials have been discussed [25]. The advantages of organic materials, in particular electrode materials, have been highlighted before [26], their perspectives in all-solid-state sodium-ion batteries have been examined in [27].

Different from sodium potassium intercalates/deintercalates reversibly into/out of graphite making the transition from lithium-ion towards potassium-ion possibly much simple [5,28]. Prospects of materials for potassium-ion batteries have been examined [29–33], positive materials were the subject [34], an early overview provides [35], perspectives and challenges have been highlighted recently in [36,37] and earlier in [38]. Further overviews are available [39–42]. Negative electrode materials for these batteries have been reviewed [43–45], particular attention to layered materials was in the focus of another review [46,47], whereas battery-type materials have been inspected in [48]. Layered materials as positive electrode materials for these batteries have been inspected elsewhere [49], and further materials in [50]. A focus on non-aqueous systems has been provided in [39,51]. Ether-based electrolyte (solutions) have been reviewed [52], design concepts for organic electrolytes have been discussed [53]. Perspectives of organic materials for potassium-ion batteries have been in the focus of reviews [54,55]. An outlook on perspectives of potassium-ion batteries is available [56].

2.2. Divalent Cations

Divalent metal-ion batteries (with Zn^{2+}, Mg^{2+}, and Ca^{2+}) have also attracted tremendous interest in the past decades due to their two-electron transfer which can lead to a higher theoretical capacity and a cell with higher energy density. They are suggested as the most promising post-lithium candidates. The working mechanism of these batteries is similar to LIBs, multivalent cations serve as charge carriers and shuttle back and forth between the negative and the positive electrode (less precisely anode and cathode) during charge-discharge.

Zinc-ion batteries (ZIBs) due to the merits of high volumetric capacity (5855 mAh·cm^{-3}) of the metal, which is almost three times that of LIBs, may enable high power density and energy density of cells, and environmental compatibility attracts rising attention as a promising alternative to LIBs. The standard potential of Zn is -0.763 V vs. SHE, but its high hydrogen overpotential permits the use of zinc metal in aqueous electrolyte solutions. The lifespan of ZIBs is still limited by the degradation of the Zn anode, in particular dendritic deposition during charging (for an overview see [57]), hydrogen evolution, and passivation layer formation during charge-discharge. Progress on zinc negative electrodes has been assessed [58], more specifically with aqueous electrolyte solutions in [59], particular attention to negative zinc electrodes in mild electrolytes has been in the focus of a review [60]. Furthermore, the number of suitable positive electrode materials to host Zn^{2+} is very limited, for overviews see [61–63], oxide-based materials have been examined in [64]. Progress and perspectives of zinc-ion batteries with aqueous electrolyte solutions has been briefly assessed [65], more general reviews are available [66–68], particular attention to pH has been paid in a report covering the whole range from acidic to alkaline [69]. Options beyond aqueous systems have been examined [70], innovative concepts are discussed in [71]. Advances in research and development of flexible zinc-ion batteries have been reviewed [72].

Magnesium-ion batteries (MIBs) and calcium-ion batteries (CIBs) are also very attractive because of the advantages derived from their divalent nature. Magnesium has a low standard electrode potential of -2.356 V vs. SHE, and a volumetric capacity (3834 mAh·cm^{-3}) almost twice that of lithium. Calcium also has a high volumetric capacity of 2072 mAh·cm^{-3}, Ca^{2+} has a large ionic radius of 1.00 Å and lower reduction potential of -2.87 V vs. SHE. Both reserves and production of magnesium and calcium are much larger than that of lithium, which makes the costs of MIBs and CIBs lower than those of LIBs. The absence of dendrite growth in MIBs and CIBs makes these batteries possibly safer than LIBs. Nevertheless, both MIBs and CIBs still face the challenges of lacking suitable positive electrode materials and lack of electrolytes compatible with electrodes. The use of metallic Mg and Ca electrodes is still not feasible in aqueous electrolyte batteries. Overviews on calcium-based secondary batteries are available [73–75]. Positive electrode materials for magnesium and magnesium-ion batteries have been reviewed [76]. Early overviews on magnesium-ion batteries are available [77,78] more recent progress on electrodes and positive electrode materials has been discussed in [79]. Advances towards practical application of magnesium-ion batteries have been discussed in [80]. Solid-state electrolytes for magnesium-ion batteries have been discussed in [81] and in [82].

Inorganic solids for dual magnesium and sodium battery electrodes have been reviewed [83].

2.3. Trivalent Cations

Aluminum ion batteries (AIBs), which are the most studied trivalent cation metal-ion batteries owing to alumnium's three-electron redox property and natural abundance of the metal, also attracted lots of researchers' attention. The working mechanism of AIBs also follows the "rocking chair" principle. The AIBs which use aqueous electrolyte solutions have the intrinsic merits of safety and lower costs, fast charging, high power and energy density. Multivalent metal cations can achieve more than one charge equivalent transferred per mole of the metal, leading to a higher specific volumetric capacity and energy density of a battery than monovalent metal-ion batteries. The corresponding specific volumetric capacity of Al is 8046 mAh·cm^{-3} which is almost four-times the value for lithium (2061 mAh·cm^{-3}).

Because Al has a fairly negative standard electrode potential (−1.676V vs. SHE), hydrogen evolution occurs prior to aluminum plating from aqueous solutions in the process of electrochemical reduction. Al metal in batteries also faces the fatal drawback of passivation layer (Al_2O_3) formation, dendrite growth, and corrosion during the charge/discharge process. Furthermore, the Al^{3+} has a relatively small ionic radius of 0.54 Å and with three positive charges a high charge density, which dramatically increases the desolvation energy barrier of Al^{3+} in the electrolyte solution. These problems so far hinder the large-scale application of the Al-based battery system. Progress on non-aqueous aluminium-ion batteries has been reviewed [84], a general review is also available [85]. Positive materials for both aqueous and non-aqueous electrolyte solutions have been handled in [86].

3. Trends and Developments

Although great developments and achievements have been realized with metal-ion batteries, several challenges shared mostly by all systems still need to be overcome both in commercial lithium-ion batteries and non-lithium metal-ion batteries, such as the insufficient specific energy, dendrite growth, and severe electrolyte solution decomposition. The trends and developments of metal ion batteries are summarized following for some of these aspects:

3.1. Cathode Materials

The energy density of a battery is affected by both the cathode and the anode, but a reliable cathode material is in many cases the more important part determining the overall performance of a battery. Even after decades of exploration, the development of cathode materials for metal-ion batteries still faces real challenges.

Currently, commercial Li-ion batteries always choose oxidic compounds as cathode materials, such as lithium cobalt oxide (LCO), lithium manganese oxide (LMO), lithium iron phosphate (LFP), lithium nickel cobalt aluminum oxide (NCA), and lithium nickel manganese cobalt oxide (NMC). The high cost and lacking sustainability have become major hindrances when choosing lithium-ion batteries as the candidate for large-scale stationary storage. In order to meet the demands of increasing cathode capacity and lowering the cost, high-voltage $LiCoO_2$ and lithium-rich layered oxide materials became much more appealing in recent years.

The cathode materials used for SIBs and PIBs have fewer options than those for LIBs, mainly layered structure transition metal oxides, polyanionic compounds, and Prussia Blue and its analogues appear to be promising. The most recent research in SIBs and PIBs has been devoted to exploring new and high-performance electrodes for high specific capacity and excellent cycle ability.

Compared with research on cathode materials for alkali metal-ion batteries, studies focused on cathode materials for multivalent metal ion batteries are still in their infancy. Because of their high charge density, the multivalent ions suffer from high migration energy barriers both in electrolyte solutions and in electrodes. The slow solid-state diffusion and sluggish desolvation process of the charge carriers are the biggest obstacles impeding progress. Only few types of material have been identified so far to serve as cathodes for rapidly and reversibly inserting/extracting the multivalent ions. The candidates are also metal oxides and metal chalcogenides with layered structures, polyanion frameworks, carbon materials, and MOF/COFs/Mxenes. Recent studies on cathode materials mainly focus on the rational design and engineering of structure, morphology, and surface texture of these cathodes. Particular challenges for electrode materials to be employed in low temperature batteries have been discussed [87], for general considerations see also [2].

3.2. Metallic Anodes

In order to meet the huge demand for high-energy storage, the research on pure metals with high specific capacity has come back to scientists' attention. Most of the metal anodes suffer from their severe intrinsic drawbacks during cycling: dendrite growth, metal corrosion, side reactions, and electrolyte decomposition. To solve these problems, design strategies of metallic anodes generally can be summarized as suppressing dendrite growth, building passivating films, and rationally designing alloys.

Dendrite growth is a notorious problem occurring on the surface of pure metal electrodes. Normally, growth has two modes, mossy and dendritic growth. The mossy metal state always forms at the very beginning; serious dendritic growth will follow with uneven metal ion concentration distribution and non-uniform electric field distribution. After repeated charge-discharge cycling, the dendrites may even puncture the separator and give rise to a short circuit. Tremendous research has been committed to finding solutions for suppressing the formation of dendrites, such as ceramic separators, polymer electrolytes, protective coating layers and 3D current collectors.

Most metal anodes, no matter whether in organic-based or aqueous-based electrolyte solutions, always face the challenge of decomposition in a highly reducing environment during the charge-discharge process. This undesirable reaction will not stop until the electrolyte solution is consumed. Hence, building a passivating film on the surface of the metal electrode, which can separate or alleviate the direct contact of the metal with the unstable electrolyte solution, was proven as an effective method to circumvent this problem and improve the battery's lifespan.

An alloy can be defined as a homogenous mix of multiple elements with metallic bonds. The introduced foreign metal can work as the 3D current collector during the charge-discharge process, the high electronic conductivity, enlarged electroactive surface, and even electrical field distribution make the alloy anode remarkably efficient in suppressing dendrite growth and alleviating the strong hydrogen evolution. Furthermore, the eutectic alloy anodes also have high corrosion resistance which can further alleviate side reactions and corrosion of the electrode. Negative alloy electrodes for potassium-ion [88] and for sodium-ion [89] batteries have been reviewed.

Conventional formation of alloys by metallurgical processes may be too energy-intensive, electrolytic processes as possible alternatives have been reviewed [90].

3.3. Electrolyte Challenges

The most studied electrolytes used for batteries can be classified into electrolyte solutions and solid-state electrolytes. All of these electrolytes have the same purpose: to provide nonflammable and highly efficient electrolytes which can enable batteries with improved safety and cycle number. General considerations regarding electrolytes for metal-ion batteries have been reported [91]. Quasi-solid and solid polymer electrolytes for multivalent metal-ion batteries have been reviewed [92].

The use of water as an electrolyte solvent provides the batteries with the advantages of low cost, nonflammable, high ionic conductivity, and enhanced kinetics. However, every coin has two sides, the water molecules which serve as solvent may be consumed during the charge-discharge process, and the decomposition of water molecules is the root of undesired side reactions. What is more, the byproducts and corrosion process will lead to the acceleration of metal anode deterioration in the following cycling. The most common strategies to improve the batteries' electrochemical performance and suppress the undesired side reactions derived from the electrolyte are categorized into three approaches: highly concentrated electrolyte (water-in-salt WiS and deep eutectic solvents DES), hydrogel electrolytes, and functional additives. Electrolyte options for zinc-ion batteries have been reviewed [93], and general strategies have been in the focus elsewhere [94].

Furthermore, investigating solid-state electrolytes (SSEs) is another promising strategy to alleviate the undesired problems. The SSE can avoid the use of organic electrolytes and enhance the safety, allow much higher cation transfer numbers, widen the potential window of stability, and prevent dendrite formation. Many studies have been conducted to evaluate suitable SSEs for metal ion batteries, which include inorganic solids, polymers, MOFs and COFs.

Theoretical methods have been applied apparently only infrequently, a first-principles approach towards magnesium-ion batteries is available [95].

4. Conclusions and Prospects

Expected volumetric and gravimetric energy densities of metal-ion batteries in particular with di- and trivalent cations suggest their use for stationary applications, given the rapidly growing demand for large scale energy storage combined with the rising use of renewable energy sources with their volatile availability this is an economically as well as ecologically attractive option.

Improvements in terms of storage capabilities, stability (both calendar and cycling) and rate capability may result in a longer run to establish these batteries as competitors for lithium-ion batteries.

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References

1. Liang, Y.; Dong, H.; Aurbach, D.; Yao, Y. Current status and future directions of multivalent metal-ion batteries. *Nat. Energy* **2020**, *5*, 646–656. [CrossRef]
2. Wu, Y.; Holze, R. *Electrochemical Energy Conversion and Storage*; Wiley-VCH: Weinheim, Germany, 2022.
3. Wu, Y.; Holze, R. Self-discharge in supercapacitors: Causes, effects and therapies: An overview. *Electrochem. Energy Technol.* **2021**, *7*, 1–37.
4. Holze, R. Self-discharge of batteries: Causes, Mechanisms and Remedies. *Adv. Mater. Sci. Technol.* **2022**. *submitted*.
5. Biemolt, J.; Jungbacker, P.; van Teijlingen, T.; Yan, N.; Rothenberg, G. Beyond lithium-based batteries. *Materials* **2020**, *13*, 425. [CrossRef]
6. Kubota, K.; Dahbi, M.; Hosaka, T.; Kumakura, S.; Komaba, S. Towards K-Ion and Na-Ion Batteries as "Beyond Li-Ion". *Chem. Rec.* **2018**, *18*, 459–479. [CrossRef]
7. Wang, Y.; Liu, D.; Sun, M.; Liu, J. Recent progress in electrode materials for aqueous sodium and potassium ion batteries. *Mater. Chem. Front.* **2021**, *5*, 7384–7402. [CrossRef]
8. Zhao, L.F.; Hu, Z.; Lai, W.H.; Tao, Y.; Peng, J.; Miao, Z.C.; Wang, Y.X.; Chou, S.L. Hard Carbon Anodes: Fundamental Understanding and Commercial Perspectives for Na-Ion Batteries beyond Li-Ion and K-Ion Counterparts. *Adv. Energy Mater.* **2021**, *11*, 2002704. [CrossRef]
9. Zhang, T.; Li, C.; Wang, F.; Noori, A.; Mousavi, M.F.; Xia, X.; Zhang, Y. Recent Advances in Carbon Anodes for Sodium-Ion Batteries. *Chem. Rec.* **2022**, *22*, e202200083. [CrossRef]
10. Lach, J.; Wróbel, K.; Wróbel, J.; Czerwński, A. Applications of carbon in rechargeable electrochemical power sources: A review. *Energies* **2021**, *14*, 2649. [CrossRef]
11. Li, M.; Du, Z.; Khaleel, M.A.; Belharouak, I. Materials and engineering endeavors towards practical sodium-ion batteries. *Energy Storage Mater.* **2020**, *25*, 520–536. [CrossRef]

12. Mauger, A.; Julien, C.M. State-of-the-art electrode materials for sodium-ion batteries. *Materials* **2020**, *13*, 3453. [CrossRef] [PubMed]
13. Yabuuchi, N.; Kubota, K.; Dahbi, M.; Komaba, S. Research development on sodium-ion batteries. *Chem. Rev.* **2014**, *114*, 11636–11682. [CrossRef] [PubMed]
14. Mass,, R.; Uchaker, E.; Cao, G. Beyond Li ion: Electrode materials for sodium and magnesium-ion batteries. In *Nanomaterials for Energy Conversion and Storage*; World Scientific: Singapore, 2017; pp. 639–755.
15. Dong, S.; Lv, N.; Wu, Y.; Zhang, Y.; Zhu, G.; Dong, X. Titanates for sodium-ion storage. *Nano Today* **2022**, *42*, 101349. [CrossRef]
16. Meng, Y.; Nie, C.; Guo, W.; Liu, D.; Chen, Y.; Ju, Z.; Zhuang, Q. Inorganic cathode materials for potassium ion batteries. *Mater. Today Energy* **2022**, *25*, 100982. [CrossRef]
17. Liu, Z.G.; Du, R.; He, X.X.; Wang, J.C.; Qiao, Y.; Li, L.; Chou, S.L. Recent Progress on Intercalation-Based Anode Materials for Low-Cost Sodium-Ion Batteries. *Chem. Sus. Chem.* **2021**, *14*, 3724–3743. [CrossRef]
18. Sarkar, S.; Roy, S.; Hou, Y.; Sun, S.; Zhang, J.; Zhao, Y. Recent Progress in Amorphous Carbon-Based Materials for Anodes of Sodium-Ion Batteries: Synthesis Strategies, Mechanisms, and Performance. *Chem. Sus. Chem.* **2021**, *14*, 3693–3723. [CrossRef]
19. Gebert, F.; Knott, J.; Gorkin III, R.; Chou, S.L.; Dou, S.X. Polymer electrolytes for sodium-ion batteries. *Energy Storage Mater.* **2021**, *36*, 10–30. [CrossRef]
20. Liu, M.; Ao, H.; Jin, Y.; Hou, Z.; Zhang, X.; Zhu, Y.; Qian, Y. Aqueous rechargeable sodium ion batteries: Developments and prospects. *Mater. Today Energy* **2020**, *17*, 100432. [CrossRef]
21. Ma, H.; Zhang, H.; Xue, M. Research Progress and Practical Challenges of Aqueous Sodium-Ion Batteries. *Acta Chim. Sin.* **2021**, *79*, 388–405. [CrossRef]
22. Hijazi, H.; Desai, P.; Mariyappan, S. Non-Aqueous Electrolytes for Sodium-Ion Batteries: Challenges and Prospects Towards Commercialization. *Batter. Supercaps* **2021**, *4*, 881–896. [CrossRef]
23. Li, Z.; Liu, P.; Zhu, K.; Zhang, Z.; Si, Y.; Wang, Y.; Jiao, L. Solid-State Electrolytes for Sodium Metal Batteries. *Energy Fuels* **2021**, *35*, 9063–9079. [CrossRef]
24. Zhang, X.; Yang, D.; Rui, X.; Yu, Y.; Huang, S. Advanced cathodes for potassium-ion battery. *Curr. Opin. Electrochem.* **2019**, *18*, 24–30. [CrossRef]
25. Chu, S.; Guo, S.; Zhou, H. Advanced cobalt-free cathode materials for sodium-ion batteries. *Chem. Soc. Rev.* **2021**, *50*, 13189–13235. [CrossRef] [PubMed]
26. Holze, R. Conjugated Molecules and Polymers in Secondary Batteries: A Perspective. *Molecules* **2022**, *27*, 546. [CrossRef]
27. Holguin, K.; Mohammadiroudbari, M.; Qin, K.; Luo, C. Organic electrode materials for non-aqueous, aqueous, and all-solid-state Na-ion batteries. *J. Mater. Chem. A* **2021**, *9*, 19083–19115. [CrossRef]
28. Komaba, S.; Hasegawa, T.; Dahbi, M.; Kubota, K. Potassium intercalation into graphite to realize high-voltage/high-power potassium-ion batteries and potassium-ion capacitors. *Electrochem. Commun.* **2015**, *60*, 172–175. [CrossRef]
29. Fan, L.; Hu, Y.; Rao, A.M.; Zhou, J.; Hou, Z.; Wang, C.; Lu, B. Prospects of Electrode Materials and Electrolytes for Practical Potassium-Based Batteries. *Small Methods* **2021**, *5*, 2101131. [CrossRef]
30. Xu, Y.S.; Duan, S.Y.; Sun, Y.G.; Bin, D.S.; Tao, X.S.; Zhang, D.; Liu, Y.; Cao, A.M. Recent developments in electrode materials for potassium-ion batteries. *J. Mater. Chem. A* **2019**, *7*, 4334–4352. [CrossRef]
31. An, Y.; Liu, Y.; Tian, Y.; Xu, X.; Ma, Y.; Wei, H.; Ma, C.; Feng, J. Recent development and prospect of potassium-ion batteries with high energy and high safety for post-lithium batteries. *Funct. Mater. Lett.* **2019**, *12*, 1930002. [CrossRef]
32. Ahmed, S.M.; Suo, G.; Wang, W.A.; Xi, K.; Iqbal, S.B. Improvement in potassium ion batteries electrodes: Recent developments and efficient approaches. *J. Energy Chem.* **2021**, *62*, 307–337. [CrossRef]
33. John, B.; Anoopkumar, V.; Mercy, T.D. Potassium-ion batteries: Key to future large-scale energy storage? *ACS Appl. Energy Mater.* **2020**, *3*, 9478–9492.
34. Wu, Z.; Zou, J.; Chen, S.; Niu, X.; Liu, J.; Wang, L. Potassium-ion battery cathodes: Past, present, and prospects. *J. Power Sources* **2021**, *484*, 229307. [CrossRef]
35. Pramudita, J.C.; Sehrawat, D.; Goonetilleke, D.; Sharma, N. An Initial Review of the Status of Electrode Materials for Potassium-Ion Batteries. *Adv. Energy Mater.* **2017**, *7*, 1602911. [CrossRef]
36. Rajagopalan, R.; Tang, Y.; Ji, X.; Jia, C.; Wang, H. Advancements and Challenges in Potassium Ion Batteries: A Comprehensive Review. *Adv. Funct. Mater.* **2020**, *30*, 1909486. [CrossRef]
37. Liu, Y.; Huang, B.; Shao, Y.; Shen, M.; Du, L.; Liao, S. Potassium-Ion Battery and Its Recent Research Progress. *Prog. Chem.* **2019**, *31*, 1329–1340.
38. Eftekhari, A.; Jian, Z.; Ji, X. Potassium Secondary Batteries. *ACS Appl. Mater. Interf.* **2017**, *9*, 4404–4419. [CrossRef]
39. Wang, B.; Ang, E.H.; Yang, Y.; Zhang, Y.; Ye, M.; Liu, Q.; Li, C.C. Post-Lithium-Ion Battery Era: Recent Advances in Rechargeable Potassium-Ion Batteries. *Chem. Eur. J.* **2021**, *27*, 512–536. [CrossRef]

40. Kim, H.; Kim, J.C.; Bianchini, M.; Seo, D.H.; Rodriguez-Garcia, J.; Ceder, G. Recent Progress and Perspective in Electrode Materials for K-Ion Batteries. *Adv. Energy Mater.* **2018**, *8*, 1702384. [CrossRef]
41. Zhang, W.; Yin, J.; Wang, W.; Bayhan, Z.; Alshareef, H.N. Status of rechargeable potassium batteries. *Nano Energy* **2021**, *83*, 105792. [CrossRef]
42. Hwang, J.Y.; Myung, S.T.; Sun, Y.K. Recent Progress in Rechargeable Potassium Batteries. *Adv. Funct. Mater.* **2018**, *28*, 1802938. [CrossRef]
43. Zhang, J.; Lai, L.; Wang, H.; Chen, M.; Shen, Z.X. Energy storage mechanisms of anode materials for potassium ion batteries. *Mater. Today Energy* **2021**, *21*, 100747. [CrossRef]
44. Li, P.; Kim, H.; Kim, K.H.; Kim, J.; Jung, H.G.; Sun, Y.K. State-of-the-art anodes of potassium-ion batteries: Synthesis, chemistry, and applications. *Chem. Sci.* **2021**, *12*, 7623–7655. [CrossRef]
45. Ma, L.; Lv, Y.; Wu, J.; Xia, C.; Kang, Q.; Zhang, Y.; Liang, H.; Jin, Z. Recent advances in anode materials for potassium-ion batteries: A review. *Nano Res.* **2021**, *14*, 4442–4470. [CrossRef]
46. Guo, K.; Wang, W.; Jiao, S. Recent progress and prospective on layered anode materials for potassium-ion batteries. *Int. J. Miner. Metall. Mater.* **2022**, *29*, 1037–1052. [CrossRef]
47. Li, W.; Bi, Z.; Zhang, W.; Wang, J.; Rajagopalan, R.; Wang, Q.; Zhang, D.; Li, Z. Advanced cathodes for potassium-ion batteries with layered transition metal oxides: A review. *J. Mater. Chem. A* **2021**, *9*, 8221–8247. [CrossRef]
48. Liu, S.; Kang, L.; Henzie, J.; Zhang, J.; Ha, J.; Amin, M.A.; Hossain, M.S.S.A.; Jun, S.C.; Yamauchi, Y. Recent Advances and Perspectives of Battery-Type Anode Materials for Potassium Ion Storage. *ACS Nano* **2021**, *15*, 18931–18973. [CrossRef]
49. Liao, J.; Han, Y.; Zhang, Z.; Xu, J.; Li, J.; Zhou, X. Recent Progress and Prospects of Layered Cathode Materials for Potassium-ion Batteries. *Energy Environ. Mater.* **2021**, *4*, 178–200. [CrossRef]
50. Ramesh, A.; Tripathi, A.; Balaya, P. A mini review on cathode materials for sodium-ion batteries. *Int. J. Appl. Ceram. Technol.* **2022**, *19*, 913–923. [CrossRef]
51. Vaalma, C.; Buchholz, D.; Passerini, S. Non-aqueous potassium-ion batteries: A review. *Curr. Opin. Electrochem.* **2018**, *9*, 41–48. [CrossRef]
52. Li, Y.; Wu, F.; Li, Y.; Liu, M.; Feng, X.; Bai, Y.; Wu, C. Ether-based electrolytes for sodium ion batteries. *Chem. Soc. Rev.* **2022**, *51*, 4484–4536. [CrossRef]
53. Mao, J.; Wang, C.; Lyu, Y.; Zhang, R.; Wang, Y.; Liu, S.; Wang, Z.; Zhang, S. Organic electrolyte design for practical potassium-ion batteries. *J. Mater. Chem. A.* **2022**, *10*. [CrossRef]
54. Zhang, W.; Huang, W.; Zhang, Q. Organic Materials as Electrodes in Potassium-Ion Batteries. *Chem. Eur. J.* **2021**, *27*, 6131–6144. [CrossRef] [PubMed]
55. Xu, S.; Chen, Y.; Wang, C. Emerging organic potassium-ion batteries: Electrodes and electrolytes. *J. Mater. Chem. A* **2020**, *8*, 15547–15574. [CrossRef]
56. Min, X.; Xiao, J.; Fang, M.; Wang, W.; Zhao, Y.; Liu, Y.; Abdelkader, A.M.; Xi, K. Potassium-ion batteries: Outlook on present and future technologies. *Energy Environ. Sci.* **2021**, *14*, 2186–2243. [CrossRef]
57. Zuo, Y.; Wang, K.; Pei, P.; Wei, M.; Liu, X.; Xiao, Y.; Zhang, P. Zinc dendrite growth and inhibition strategies. *Mater. Today Energy* **2021**, *20*, 100692. [CrossRef]
58. Liu, Y.; Liu, Y.; Wu, X. Toward Long-Life Aqueous Zinc Ion Batteries by Constructing Stable Zinc Anodes. *Chem. Rec.* **2022**, *22*, e202200088. [CrossRef]
59. Huang, J.; Qiu, X.; Wang, N.; Wang, Y. Aqueous rechargeable zinc batteries: Challenges and opportunities. *Curr. Opin. Electrochem.* **2021**, *30*, 100801. [CrossRef]
60. Yang, J.; Yin, B.; Sun, Y.; Pan, H.; Sun, W.; Jia, B.; Zhang, S.; Ma, T. Zinc Anode for Mild Aqueous Zinc-Ion Batteries: Challenges, Strategies, and Perspectives. *Nano Micro Lett.* **2022**, *14*, 42. [CrossRef]
61. Zuo, S.; Xu, X.; Ji, S.; Wang, Z.; Liu, Z.; Liu, J. Cathodes for Aqueous Zn-Ion Batteries: Materials, Mechanisms, and Kinetics. *Chem. Eur. J.* **2021**, *27*, 830–860. [CrossRef]
62. Li, C.; Zhang, X.; He, W.; Xu, G.; Sun, R. Cathode materials for rechargeable zinc-ion batteries: From synthesis to mechanism and applications. *J. Power Sources* **2020**, *449*, 227596. [CrossRef]
63. Wang, X.; Zhang, Z.; Xi, B.; Chen, W.; Jia, Y.; Feng, J.; Xiong, S. Advances and Perspectives of Cathode Storage Chemistry in Aqueous Zinc-Ion Batteries. *ACS Nano* **2021**, *15*, 9244–9272. [CrossRef]
64. Zhou, Y.; Chen, F.; Arandiyan, H.; Guan, P.; Liu, Y.; Wang, Y.; Zhao, C.; Wang, D. Oxide-based cathode materials for rechargeable zinc ion batteries: Progresses and challenges. *J. Energy Chem.* **2021**, *57*, 516–542. [CrossRef]
65. Ma, N.; Wu, P.; Wu, Y.; Jiang, D.; Lei, G. Progress and perspective of aqueous zinc-ion battery. *Funct. Mater. Lett.* **2019**, *12*, 1930003. [CrossRef]
66. Xu, W.; Wang, Y. Recent Progress on Zinc-Ion Rechargeable Batteries. *Nano Micro Lett.* **2019**, *11*, 90. [CrossRef] [PubMed]

67. Tang, B.; Shan, L.; Liang, S.; Zhou, J. Issues and opportunities facing aqueous zinc-ion batteries. *Energy Environ. Sci.* **2019**, *12*, 3288–3304. [CrossRef]
68. Zhang, X.; Hu, J.P.; Fu, N.; Zhou, W.B.; Liu, B.; Deng, Q.; Wu, X.W. Comprehensive review on zinc-ion battery anode: Challenges and strategies. *InfoMat* **2022**, *4*, e12306. [CrossRef]
69. Wang, N.; Wan, H.; Duan, J.; Wang, X.; Tao, L.; Zhang, J.; Wang, H. A review of zinc-based battery from alkaline to acid. *Mater. Today Adv.* **2021**, *11*, 100149. [CrossRef]
70. Lv, Y.; Xiao, Y.; Ma, L.; Zhi, C.; Chen, S. Recent Advances in Electrolytes for "Beyond Aqueous" Zinc-Ion Batteries. *Adv. Mater.* **2022**, *34*, 2106409. [CrossRef]
71. Borchers, N.; Clark, S.; Horstmann, B.; Jayasayee, K.; Juel, M.; Stevens, P. Innovative zinc-based batteries. *J. Power Sources* **2021**, *484*, 229309. [CrossRef]
72. Xu, Y.; Xu, X.; Guo, M.; Zhang, G.; Wang, Y. Research Progresses and Challenges of Flexible Zinc Battery. *Front. Chem.* **2022**, *10*, 827563. [CrossRef]
73. Ouchi, T.; Kim, H.; Spatocco, B.L.; Sadoway, D.R. Calcium-based multi-element chemistry for grid-scale electrochemical energy storage. *Nat. Commun.* **2016**, *7*, 10999. [CrossRef] [PubMed]
74. Ji, B.; He, H.; Yao, W.; Tang, Y. Recent Advances and Perspectives on Calcium-Ion Storage: Key Materials and Devices. *Adv. Mater.* **2021**, *33*, 2005501. [CrossRef] [PubMed]
75. Gummow, R.J.; Vamvounis, G.; Kannan, M.B.; He, Y. Calcium-Ion Batteries: Current State-of-the-Art and Future Perspectives. *Adv. Mater.* **2018**, *30*, 1801702. [CrossRef] [PubMed]
76. Huie, M.M.; Bock, D.C.; Takeuchi, E.S.; Marschilok, A.C.; Takeuchi, K.J. Cathode materials for magnesium and magnesium-ion based batteries. *Coord. Chem. Rev.* **2015**, *287*, 15–27. [CrossRef]
77. Saha, P.; Datta, M.K.; Velikokhatnyi, O.I.; Manivannan, A.; Alman, D.; Kumta, P.N. Rechargeable magnesium battery: Current status and key challenges for the future. *Prog. Mater. Sci.* **2014**, *66*, 1–86. [CrossRef]
78. Foot, P.J.S. Principles and prospects of high-energy magnesium-ion batteries. *Sci. Prog.* **2015**, *98*, 264–275. [CrossRef]
79. Rashad, M.; Asif, M.; Wang, Y.; He, Z.; Ahmed, I. Recent advances in electrolytes and cathode materials for magnesium and hybrid-ion batteries. *Energy Storage Mater.* **2020**, *25*, 342–375. [CrossRef]
80. Medina, A.; Pérez-Vicente, C.; Alcántara, R. Advancing towards a practical magnesium ion battery. *Materials* **2021**, *14*, 7488. [CrossRef]
81. Guo, M.; Yuan, C.; Zhang, T.; Yu, X. Solid-State Electrolytes for Rechargeable Magnesium-Ion Batteries: From Structure to Mechanism. *Small* **2022**, *18*, 2106981. [CrossRef]
82. Jaschin, P.W.; Gao, Y.; Li, Y.; Bo, S.H. A materials perspective on magnesium-ion-based solid-state electrolytes. *J. Mater. Chem. A* **2020**, *8*, 2875–2897. [CrossRef]
83. Rubio, S.; Medina, A.; Cabello, M.; Lavela, P.; Alcántara, R.; Vicénte, C.P.; Ortiz, G.F.; Tirado, J.L. Inorganic solids for dual magnesium and sodium battery electrodes. *J. Solid State Electr.* **2020**, *24*, 2565–2573. [CrossRef]
84. Craig, B.; Schoetz, T.; Cruden, A.; Ponce de Leon, C. Review of current progress in non-aqueous aluminium batteries. *Renew. Sustain. Energy Rev.* **2020**, *133*, 110100. [CrossRef]
85. Das, S.K.; Mahapatra, S.; Lahan, H. Aluminium-ion batteries: Developments and challenges. *J. Mater. Chem. A* **2017**, *5*, 6347–6367. [CrossRef]
86. Ru, Y.; Zheng, S.; Xue, H.; Pang, H. Different positive electrode materials in organic and aqueous systems for aluminium ion batteries. *J. Mater. Chem. A* **2019**, *7*, 14391–14418. [CrossRef]
87. Pang, X.; An, B.; Zheng, S.; Wang, B. Cathode materials of metal-ion batteries for low-temperature applications. *J. Alloys Compd.* **2022**, *912*, 165142. [CrossRef]
88. Suo, G.; Cheng, Y.; Zhang, J.; Ahmed, S.M. Recent Progress and Perspectives on Alloying Anodes for Potassium-Ion Batteries. *Chem. Nano Mat.* **2021**, *7*, 1291–1308. [CrossRef]
89. Zheng, S.M.; Tian, Y.R.; Liu, Y.X.; Wang, S.; Hu, C.Q.; Wang, B.; Wang, K.M. Alloy anodes for sodium-ion batteries. *Rare Met.* **2021**, *40*, 272–289. [CrossRef]
90. Li, X.Y.; Qu, J.K.; Yin, H.Y. Electrolytic alloy-type anodes for metal-ion batteries. *Rare Met.* **2021**, *40*, 329–352. [CrossRef]
91. Erickson, E.M.; Markevich, E.; Salitra, G.; Sharon, D.; Hirshberg, D.; De La Llave, E.; Shterenberg, I.; Rozenman, A.; Frimer, A.; Aurbach, D. Development of advanced rechargeable batteries: A continuous challenge in the choice of suitable electrolyte solutions. *J. Electrochem. Soc.* **2015**, *162*, A2424–A2438. [CrossRef]
92. Lu, J.; Jaumaux, P.; Wang, T.; Wang, C.; Wang, G. Recent progress in quasi-solid and solid polymer electrolytes for multivalent metal-ion batteries. *J. Mater. Chem. A* **2021**, *9*, 24175–24194. [CrossRef]
93. Liu, C.; Xie, X.; Lu, B.; Zhou, J.; Liang, S. Electrolyte Strategies toward Better Zinc-Ion Batteries. *ACS Energy Lett.* **2021**, *6*, 1015–1033. [CrossRef]

94. Yan, H.; Zhang, X.; Yang, Z.; Xia, M.; Xu, C.; Liu, Y.; Yu, H.; Zhang, L. Insight into the electrolyte strategies for aqueous zinc ion batteries. *Coord. Chem. Rev.* **2022**, *452*, 214297. [CrossRef]
95. Wu, X.; Dou, Y.; Lian, R.; Wang, Y.; Wie, Y. Understanding rechargeable magnesium ion batteries via first-principles computations: A comprehensive review. *Energy Storage Mater.* **2022**, *48*, 344–355. [CrossRef]