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Xie, Jian; Zhang, Qichun

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Recent Progress in Multivalent Metal (Mg, Zn, Ca & Al) and Metal-Ion Rechargeable Batteries with Organic Materials as Promising Electrodes

*Jian Xie, Qichun Zhang**

Dr. J. Xie, Prof. Q. Zhang
School of Materials Science and Engineering
Nanyang Technological University (Singapore)
639798 Singapore
E-mail: qczhang@ntu.edu.sg

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Abstract: The emerging demand for electronic and transportation technologies has driven the development of rechargeable batteries with enhanced capacity storage. Especially, multivalent metal (Mg, Zn, Ca & Al) and metal-ion batteries have recently attracted considerable interests as promising substitutes for future large-scale energy storage devices, due to their natural abundance and multi-electron redox capability. These alkaline metals are compatible with non-flammable aqueous electrolytes and are less reactive when exposed in ambient atmosphere as compared with Li metals, hence enabling potential safer battery systems. Luckily, green and sustainable organic compounds could be designed and tailored as universal host materials to accommodate multivalent metal ions. Considering these advantages, effective approaches toward achieving organic multivalent metal and metal-ion rechargeable batteries are highlighted in this review. Moreover, organic structures, cell configurations and key relevant electrochemical parameters are presented. Hopefully, this review will provide a fundamental guidance for future development of organic-based multivalent metal and metal-ion rechargeable batteries.

1. Introduction

To pursue next-generation of rechargeable batteries with higher energy density, better safety and lower cost, the development of battery systems beyond Li-ion configuration is essentially desirable.^[1-3] In the past two decades, numerous efforts on rechargeable multivalent metal batteries have been focused on inorganic electrodes, particularly those materials based on conventional insertion mechanisms.^[4-11] However, considering from the standpoints of capacity storage and energy density, there is little room for further improvement of inorganic materials. Therefore, the discovery of new redox chemistries between host materials and charge carriers is essentially desirable. According to the theoretical capacity calculation,^[12] the charge storage of electrode materials can be either improved from the reduction of molecular weight or the adoption of multi-redox mechanisms. Fortunately, organic materials satisfy both requirements, as they consist of low-weight atoms and can be flexibly designed with multi-redox ability.^[13-18] Moreover, organic compounds can be tailored as universal host electrode materials for the storage of both monovalent ions (either anions or cations) and multivalent metal-ions.^[19-21]

In the early stage, exploration of organic-electrode-based multivalent metal batteries mainly focused on p-type conductive polymers with extended π -conjugation, particularly polyaniline (PANI), polypyrrole (PPy) and polythiophene (PTh).^[22-24] Organosulfurs^[25] and nitroxide radicals^[26-29] were later introduced, however, the serious dissolution issue and limited electron transfer hinder their future applications. Recently, aiming at improving the electrochemical performance of organic electrodes, several attempts have been extended to n-type carbonyl-containing compounds,^[30-31] due to their structural diversity and electrochemical stability. Moreover, this type of organic materials on the basis of coordination chemistry starts to dominate the current research. Nevertheless, challenges associated with the

poor reversibility/cyclability, low output voltage, and large polarization for multivalent metal and metal-ion rechargeable batteries are still present and need to be solved.

To gain insight into these issues, effective approaches are encouraged to be proposed to improve the current situation of organic-electrode-based multivalent metal and metal-ion batteries. Actually, recent successful strategies from organic lithium (Li) ion batteries based on conductive polymers,^[32-33] conjugated polymers,^[34-40] carbonyl compounds,^[41-49] and new redox-chemistry compounds,^[50-57] afford us sufficient experiences that merit attention. Innovative demonstrations including all-organic-electrode and all-solid-state batteries have also been realized based on these materials.^[55, 58-61] Moreover, due to the distinct superiorities including enlarged surface area, enhanced electrochemical reactivity and shortened pathway for charge transfer that could be provided by nanostructures, valuable experience from Li-ion batteries on organic nanostructures (e.g. conductive polymers,^[62-63] conjugated polymers^[34-35] and covalent organic frameworks^[64]) could provide opportunities for organic multivalent batteries to achieve improved electrochemical performance. However, the progress on organic multivalent metal and metal-ion batteries is still in its preliminary stage. There remains much space to optimize the electrochemical performance of organic electrodes along with the development of appropriate electrolyte systems. Since there is still lack of a review that systematically covers the state-of-the-art developments of organic multivalent metal and metal-ion rechargeable batteries, we herein provide an overview on effective organic electrode materials for promising high-performance multivalent metal and metal-ion batteries. The existing configurations of organic multivalent metal and metal-ion rechargeable batteries are introduced, followed by a comprehensive discussion regarding the recent developments on a wide range of organic compounds. These materials are further classified into four distinct categories: Magnesium (Mg), Zinc (Zn), Calcium (Ca), and Aluminum (Al) batteries according to their configurations. Through this review, we aim to provide a fundamental

guidance for future designing and development of organic multivalent metal and metal-ion rechargeable batteries.

2. Overview of Organic Multivalent Metal & Metal-Ion Rechargeable Batteries

Table 1 lists the chemical structures of representative organic compounds that have been recently demonstrated for multivalent metal and metal-ion rechargeable batteries. Key parameters including the charge-storage method, electrolyte, capacity, voltage window and cycling stability are presented. In consideration of the typical two-electrode systems, organic multivalent rechargeable batteries can be classified into two major classes. One class is the half-cell configuration that uses pure metals (e.g. Mg, Zn, Ca & Al) as the counter electrodes. This class is also considered as metal-organic battery associating with the shuttling of either cations or anions. To be noted that, the reversible stripping and plating capability of multivalent metal ions is the key to achieve high reversibility and long-lasting performance for such a battery system. The other class is the full-cell configuration (metal-ion battery) associating with the shuttling of metal cations. For this class, the need of a metal counter electrode is not a necessary. Instead, the counter electrode that provides multivalent metal-ions is usually a host material pre-treated through the insertion of metal ions (e.g. activated carbons, inorganic materials, etc.). It is worth mentioning that other than multivalent metal ions, most organic compounds presented in Table 1 have been previously investigated versus Li metal, revealing the universal properties of organic materials to accommodate a series of metal ions. With further explorations on compatible and suitable electrolyte solutions, more organic materials are believed to be demonstrated versus multivalent metals in the near future.

3. Organic Electrodes for Rechargeable Mg & Mg-Ion Batteries

Among various types of organic compounds, conductive polymers have been comprehensively recognized as redox-active compounds for rechargeable Li batteries based on the anion-insertion mechanism (p-type).^[22, 65-66] Because of the good redox reversibility, conductive polymer is among the early class of active materials for Mg-ion batteries. PANI **1** was a typical example. In 1996, Mg/PAN cells were fabricated with the addition of a series of aqueous magnesium salts as the electrolytes.^[24] The average operating potentials of the Mg/PANI cells are in the range of 1.1-1.4 V. Other than Mg-ion batteries, this prototype is more preferred to be an anion-dominated battery, since anions (ClO^- , Cl^- and Br^-) were reported to be doped into and stored by PANI **1** at the cathode side. And, typical redox peaks could be noticed from the cyclic voltammogram of PANI in the electrolyte solution. Although this demonstration delivered limited electrochemical results, it reveals the potential of conductive polymers as promising electrodes for Mg batteries. However, in contrast to Li batteries, limited attentions have been devoted into developing conductive polymer-based Mg batteries. With the increasing investigations, future rechargeable Mg batteries with appropriate conductive polymers are expected to be achieved.

Organosulfur is another type (n-type) of redox-active organic electrodes, attributing to the reversible cleavage and the formation of disulfide bonds (S-S).^[67] NuLi et al. first investigated a series of organosulfurs: 2,5-dimercapto-1,3,4-thiadiazole (DMcT) **2**, poly-2,2'-dithiodianiline (PDTDA) **3**, and a conductive sulfur-containing material (CSM) **4** as cathode materials for Mg batteries.^[25] Inspired by the molecular-level mixing approach between conductive polymer and organosulfur,^[68] a composite electrode between DMcT **2** and PANI was obtained and applied as a cathode. Although obvious voltage plateaus could be observed on the composite DMcT-PANI (Figure 1a), a low capacity of 27.2 mAh g⁻¹ (vs. Mg) was achieved after 26 cycles (Figure 1b). To further improve the capacity, PDTDA **3**, a compound containing both S-S bond and aniline moiety, was later investigated. As compared with DMcT-PANI/Mg, this PDTDA /Mg cell could reach an enhanced capacity of 78 mAh g⁻¹

(Figure 1c), attributing to the better electrocatalytic effect originated from the intramolecular aniline as well as the conductive behavior of this compound. From the perspective of molecular designing, the authors considered that CSM **4**, with a co-planar conjugated backbone and C-S-S-C bond, could be a better choice. CSM **4** was previously reported to be simply synthesized through heating the mixture of polyacrylonitrile and sublimed sulfur at 450 °C.^[69] In the study, by further adding PANI, a CSM-PANI composite was obtained. This composite electrode exhibited a high initial capacity of 117.3 mAh g⁻¹ (vs. Mg), with a retention of about 78% after 22 cycles. In the following work, NuLi et al. further developed several carbyne polysulfides (with diameters of several hundred nanometers) by heating carbyne and sulfur at different temperatures.^[70] Nevertheless, the electrochemical performance of the as-fabricated carbyne polysulfide/Mg cell was not satisfactory in terms of capacity and cycling stability (Figure 1d), probably due to the slow kinetic of electrolyte species diffused into the porous material. Although these demonstrations suggest the feasibility of organosulfurs to be used as active materials for rechargeable Mg batteries, the recombination efficiencies of S-S bonds versus Mg were still low. This could result in low reversibility and poor stability (usually less than 30 cycles) of these materials during the continuous charging and discharging. Regarding these disadvantages as well as the dissolution nature of organosulfurs, the research on organosulfurs seems to be stagnant and limited to aforementioned investigations.

Apart from organosulfurs, radical polymers have been proven to be stable electrodes for fast charge-discharge organic-based Li batteries in the past two decades.^[71] Nevertheless, previous successful strategies on radical polymers for Li batteries might not be suitable for Mg batteries, due to the sluggish kinetics of compatible Mg electrolyte systems during redox reactions.^[26-27] For example, a nanocomposite electrode consisting of poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA) (~10 nm) **5** and graphene was reported to suffer from low capacity, large polarization and rapid capacity fading upon Mg²⁺ insertion,

even at a small current density.^[26] In addition, this nanocomposite was discovered to operate at a low voltage window of 0.3-1.8 V in 0.25 M $\text{Mg}(\text{AlCl}_2\text{EtBu})_2$ /tetrahydrofuran (THF). Since output voltage is also a critical parameter toward high energy density batteries, a promising electrolyte system containing 0.3 M magnesium(II) bis(trifluoromethane sulfonyl)imide ($\text{Mg}(\text{TFSI})_2$) in glyme/diglyme was developed to further improve the output voltage of PTMA **5**.^[27] Such an electrolyte was stable at a high voltage window of 1.75-3.4 V for a PTMA/Mg battery (Figure 2a-b). However, capacity fading was still observed due to partial dissolution of PTMA **5** in the electrolyte upon anion insertion. Learning from these experiences, future studies are encouraged to be devoted into developing compatible Mg-containing electrolyte systems for improved electrochemical performance of radical polymers.

In the pursuit of high-performance organic materials, carbonyl-containing compounds (e.g. redox-active quinones, anhydrides and imides) have recently attracted intensive research interest.^[41] Carbonyl compounds could be easily designed with multi-electron redox characteristics, and they have been demonstrated to show high structural stability through either the coordination method to accommodate alkali monovalent metal ions or the intermolecular interaction to accommodate multivalent metal ions.^[19-21, 72-73] Advantages of carbonyl compounds including fast redox capability, good structural stability, and high storage endow organic batteries with outstanding performance.^[13] Most particularly, the excellent compatibility of carbonyl-containing compounds with different electrolyte species have been widely accepted.^[41] As a pioneer carbonyl candidate for rechargeable Mg batteries, 2,5-dimethoxy-1,4-benzoquinone (DMBQ) **6** was examined by using 0.5 M $\text{Mg}(\text{ClO}_4)_2/\gamma$ -butyrolactone as the electrolyte solution.^[30] Although ionic salts like $\text{Mg}(\text{ClO}_4)_2$ has been contentiously considered to show low or no compatibility with Mg metal due to the almost impossible Mg stripping and plating,^[74-75] the as-fabricated three-electrode-cell (DMBQ/Mg ribbon/Mg wire) in this electrolyte still delivered a high initial Mg^{2+} capacity storage of 260 mAh g^{-1} with an average output voltage of 0.9 V (vs. Mg_{quasi} as defined in the study) (Figure

2c). Two distinct plateaus could be clearly observed from the charge and discharge profiles, suggesting a low polarization of DMBQ **6** during the redox reactions. This study reveals a bright future of organic Mg batteries based on the carbonyl reduction and oxidation chemistry through intermolecular interaction. Later, a series of sulfone-based electrolyte solutions (sulfolane, ethyl-*i*-propyl sulfone and di-*n*-propyl sulfone in 0.5 M magnesium $\text{Mg}(\text{TFSI})_2$) were examined versus DMBQ **6** by the same group.^[31] Nonetheless, the as-fabricated DMBQ/Mg cell consisting of 0.5M $\text{Mg}(\text{TFSI})_2$ in sulfolane only provided a maximum capacity of about 100 mAh g⁻¹ accompanied by a large overpotential (Figure 2d). Chen et al. also investigated the cell performance of DMBQ **6** versus Mg metal, but with two non-nucleophilic electrolyte systems, $\text{Mg}(\text{TFSI})_2$ -2MgCl₂ in dimethoxyethane (DME) and $\text{Mg}(\text{TFSI})_2$ in diglyme.^[76] Both electrolytes showed the occurrence of reversible Mg plating and stripping, whereas the latter one presented a large overpotential with a low Coulombic efficiency (CE) of 58.8%, which is much lower than the former one with an excellent CE close to 100%. As a result, the DMBQ/Mg cell equipped with 0.5 M $\text{Mg}(\text{TFSI})_2$ -2MgCl₂ in DME delivered a higher average voltage larger than 2.0 V and a much-improved initial capacity of 226 mAh g⁻¹ (Figure 2e) as compared with the cell equipped with 0.5 M $\text{Mg}(\text{TFSI})_2$ in diglyme. Both cells showed some certain degree of capacity fading after 30 cycles (Figure 2f, cycling stability of the former cell), likely due to the dissolution of DMBQ **6**.

To overcome the dissolution behavior of carbonyl-containing compounds from the aspect of molecular tuning, the common method is through the polymerization of small carbonyl molecules to obtain polymers with some limited solubility.^[77] In particular, quinones and anhydrides in their polymer forms show significantly enhanced capacity storage and cycling stability as compared with their small-molecule forms.^[78-79] As frequently-investigated organic electrodes for rechargeable Li batteries, anthraquinone-based polymers also attracted many research efforts on rechargeable Mg batteries. Dominko et al. demonstrated an

interesting study by testing poly(anthraquinone sulfide) (PAQS) **7** with different non-nucleophilic electrolytes. Mg foil and modified Mg powder (200-500 nm nanoparticles) anodes were investigated as the counter electrodes.^[77] The capacity provided by the PAQS/Mg powder cell was 50% higher than that provided by the PAQS/Mg foil cell. This was attributed to the greatly enhanced kinetics of Mg powder as compared with Mg foil anode during the electrochemical reaction. By further optimizing the electrolyte solution, the as-fabricated PAQS/Mg powder cell with 0.37 M MgCl₂ and 0.15 M Mg(TFSI)₂ in THF/glyme = 3 : 2 (vol.%) (MTCC) delivered a high initial capacity of 225 mAh g⁻¹ (Figure 3a), which was very close to the theoretical capacity of PAQS **7**. However, gradual deterioration of PAQS **7** was observed during the cycling (inset of Figure 3a). Inspired by the strategy that different linking methods of anthraquinone monomers could lead to different electrochemical behaviors of polymer electrodes (vs. Li metal),^[80] Chen et al. carried out an investigation on the Mg battery performance of two poly(anthraquinone) derivatives: poly(1,4-anthraquinone) (14PAQ) **8** and poly(2,6-anthraquinone) (26PAQ) **9**.^[78] In contrast to the sharp capacity decay of PAQS **7**, 14PAQ **8** and 26PAQ **9** provided greatly-improved stability and long-term cycling. Particularly, a high capacity of 104.9 mAh g⁻¹ could be achieved after 100 cycles by the 14PAQ/Mg cell, with negligible capacity decay (versus the 7th cycle) (Figure 3b). More importantly, a reduced polarization (Figure 3c) was observed due to the smaller highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap of 14PAQ **8** as compared with these of PAQS **7** and 26PAQ **9**. This study proposed a feasible concept to improve the cycling stability of polymer electrodes through structure tailoring. Other than solely considering quinones as the building blocks, a poly(hydrobenzoquinonyl-benzoquinonyl sulfide) polymer (PHBQS) **10** was prepared through a solvothermal method.^[81] PHBQS **10** consisting of both benzoquinone and hydroquinone units could provide an average output voltage of 2.0 V and a capacity of about 140 mAh g⁻¹ after 25 cycles when assembled versus Mg powder anode (Figure 3d).

Considering the advantages such as high safety, non-flammable property, low cost and non-toxicity of aqueous electrolytes, many investigations on organic electrode materials by using such electrolyte systems have been conducted. As an attractive organic small molecule for Li batteries, the planar structured pyrene-4,5,9,10-tetraone (PTO) could undergo multi-electron reactions with a good reversibility.^[82] To be highlighted that, PTO is one of the best-performed single small-molecules with high capacities (Figure 3e). Due to these superiorities, the polymerized form of PTO, namely, PPTO **11**, was obtained and used as an anode coupled with a Prussian blue cathode.^[20] The PPTO/magnesiated copper hexacyanoferrate (Mg_xCuHCF) full-cell added with an aqueous 4.5 M $\text{Mg}(\text{NO}_3)_2$ exhibited an initial capacity of 144 mAh g^{-1} with a retention of 66% after 1000 cycles (Figure 3f).

Besides the quinone-based compounds discussed above, an anhydride compound was also demonstrated to show the ability to reversibly store Mg-ions in aqueous electrolyte systems.^[83] The small molecule 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) **12**, which has been widely observed to store monovalent Li^+ ,^[84] Na^+ ,^[85] K^+ ,^[86] H_3O^+ ^[87] and NH_4^+ ^[88], was also demonstrated as an excellent host material to store Mg^{2+} in a saturated aqueous 4.8 M $\text{Mg}(\text{NO}_3)_2$ environment.^[83] The PTCDA **12** crystal shows a submicron rod structure with a diameter and length of around 400 nm and 1.2 μm , respectively. It was observed to undergo unique expansion and contraction along different crystallographic directions during the insertion of Mg^{2+} (Figure 3g). The as-assembled three-electrode-cell deploying PTCDA **12**, activated carbon and Ag/AgCl as the working, counter and reference electrode, respectively, exhibited good rate stability since a large capacity of 75 mAh g^{-1} at 500 mA g^{-1} was achieved. (Figure 3h). Because Mg metal was not used in such a cell configuration, the Mg-ions inserted into PTCDA **12** were therefore merely provided by the electrolyte. This discovery reveals a new Mg^{2+} storage mechanism on the basis of the evolution effects on organic crystal structures.

Moreover, through the polymerization of anhydrides with amines, several polyimides were obtained and used as stable electrodes for Mg batteries by several groups.^[21, 79, 89-90] Successful studies have been mainly focused on those polymers obtained from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) and pyromellitic dianhydride (PMDA) building blocks. For example, Dominko et al. evaluated a naphthalene-hydrazine polyimide (NP) **13** obtained from NTCDA.^[90] However, a low capacity corresponding to 42% of NP's theoretical value **13** was delivered. Xia et al. also investigated a NTCDA-based polyimide **14**.^[79] When assembled into a three-electrode cell with 1 M MgSO₄ aqueous electrolyte, **14** delivered a large capacity of 140 mAh g⁻¹. An excellent retention of 90% could be maintained after 2000 cycles (Figure 4a). More importantly, a fast discharge process could be completed in only 43 seconds with a high capacity of 120 mAh g⁻¹, indicating the potential application of **14** as a fast charge-discharge electrode. By further incorporating **14** into a full-cell with an inorganic cathode nickel hexacyanoferrate, a good redox reversibility was also observed from this organic-inorganic full-cell. Wang et al. reported the development of a composite, named PPMDA@MCNTs, based on a PMDA-based polyimide **15** and multiwall carbon nanotubes (Figure 4b).^[89] The composites exist in nanosheet layers with an average thickness of around 10 nm. By adding a concentrated Mg(TFSI)₂/MgSO₄ aqueous electrolyte with expanded electrochemical stability window, the three-electrode cell delivered an initial capacity of 110 mAh g⁻¹ between 1.7 and 2.5 V with an excellent retention of 87% after 500 cycles (Figure 4c). Even under a high current rate of 20 C, the cell could provide a large capacity approximate to 85 mAh g⁻¹. To further assess the stability of PPMDA **15**, an aqueous Mg-ion full-cell based on PPMDA **15** and an inorganic cathode Li₃V₂(PO₄)₃ (LVP) was developed. Surprisingly, such an aqueous PPMDA/LVP full-cell showed an outstanding capacity retention of 92% after 6000 cycles, which is among the best-performed Mg-ion batteries. The sluggish diffusion of Mg²⁺ in traditional non-aqueous electrolytes was believed to be accelerated in such an aqueous system. In their subsequent work, the electrochemical

superiority of micro-sized **15** (named PI@CNT) was not only confirmed by a non-aqueous based rechargeable Mg battery, but also confirmed by an ionic liquid based rechargeable Al battery.^[21] The results reveal the versatile property of **15** to be used as a universal organic material for multivalent metal rechargeable batteries. Wu et al. demonstrated that, when coupling perylene diimide-ethylene diamine (PDI-EDA) **16** with a p-type conductive polymer polytriphenylamine (PTPAn), a dual-ion all-organic-electrode battery could be developed (Figure 4d).^[91] PDI-EDA and PTPAn particles were presented in the range of several hundred nanometers to micrometers. $\text{Mg}(\text{ClO}_4)_2$ in anhydrous acetonitrile was prepared as the electrolyte solution, which provides both the Mg^{2+} and ClO_4^- ions to be reversibly transferred during the reactions. Impressively, such an all-organic-electrode battery delivered a stable capacity of around 80 mAh g^{-1} and lasted for 5000 cycles with an excellent capacity retention of 88% (Figure 4e).

Differing from aforementioned polymerization strategy, another attempt to overcome the dissolution issue of organic electrodes is through the synthesis of organic salts.^[92-94] Because the formation of alkali-metal-oxygen bond could greatly reduce the solubility of organic compounds in common electrolytes. As an emerging class of organic compounds with high-density carbonyl groups, rhodizonate salts have received considerable interests for rechargeable Li, Na, and K batteries.^[19, 93, 95-96] Building on these successful experiences, an innovative Mg battery consisting of dual salts has been very recently achieved based on sodium rhodizonate ($\text{Na}_2\text{C}_6\text{O}_6$) **17** nanocrystals and Mg anode.^[97] The widths of the nanocrystals obtained with different morphologies are in the range of 200 nm - 1 μm . Figure 4f shows the crystal structure of $\text{Na}_2\text{C}_6\text{O}_6$ **17**. A hybrid Mg-Li electrolyte (0.25 M all-phenyl complex (APC) and 1 M LiCl) was used as the dual salts. Although the reaction was dominantly driven by Li^+ , the co-intercalation of Mg^{2+} was an advantage to alleviate the exfoliation of C_6O_6 layers. As a result, high capacities of 450 and 175 mAh g^{-1} were achieved at the current densities of 0.05 and 5 A g^{-1} , respectively, though more than 60% of the

capacity was found to be originated from the pseudocapacitive contribution. To be noted that, organic crystals have been seldom investigated on multivalent metal-ion batteries. This study successfully revealed the crystal structure changes of organic crystals upon the insertion of Mg^{2+} .

Except for the demonstrations on organic compounds as active electrode materials, a recent proof-of-concept study revealed the effectiveness of an organic artificial interphase, enabling the reversible Mg deposition and stripping in carbonate-based electrolyte.^[98] The interphase was made from thermally-cyclized polymeric polyacrylonitrile (cPAN) and Mg triflate (Figure 4g). It appeared to be a polymeric coating with a thickness of about 100 nm. Such an interphase coated onto the surface of Mg powders successfully prevented the decomposition of carbonate-based electrolyte, therefore leading to superior performance of a V_2O_5 /interphase-coated Mg cell. This study opens a window to promote the electrochemical performance of Mg batteries from the perspective of electrode interphase engineering.

Other than bare Mg^{2+} insertion chemistry, a recent study revealed a hybrid-ion insertion of both solvated MgCl^+ and Mg^{2+} in carbonyl compounds when using MgCl_2 -based electrolytes (Figure 5a-b).^[99] This observation indicates that almost all previously reported carbonyl compounds in MgCl_2 -based electrolytes were actually dominantly driven by MgCl^+ insertion. By switching the electrolyte to a chloride-free system ($\text{Mg}(\text{TFSI})_2$ in diglyme), DMBQ **6** and 14PAQ **8** delivered much enhanced gravimetric energy density. Conjugated redox polymer P(NDI2OD-T2) **18** was also assessed and delivered excellent cycling and rate stability in the chloride-free electrolyte (Figure 5c-d). This study provides an opportunity to direct the hybrid-ion storage chemistry to a real divalent Mg^{2+} storage chemistry, enabling higher energy densities of future organic-based Mg batteries.

4. Organic Electrodes for Rechargeable Zn & Zn-Ion Batteries

Attributing to the high theoretical gravimetric capacity (820 mAh g^{-1}) and low redox potential (-0.76 V vs. Standard Hydrogen Electrode (NHE)) of Zn anode without the obvious hydrogen evolution, rechargeable Zn batteries have also gained considerable efforts. Particularly, aqueous Zn batteries stand out due to the good compatibility between Zn and aqueous electrolytes.^[8, 100] The low capacity storage, poor ionic conductivity, and high activation energy associated with the interfacial charge transfer of nonaqueous electrolyte based batteries could be effectively solved by the replacement of aqueous electrolytes.^[8-9, 101] Similar to other battery systems (e.g. Li, Mg), historical studies regarding rechargeable Zn batteries began with the investigations of conductive polymers, particularly PANI.^[102-103] Since then, many demonstrations on PANI-based rechargeable Zn batteries with different strategies have been reported.^[104-114] For example, the assembled Zn/PANI cell in chloride and bromide media showed an initial capacity of 100 mAh g^{-1} ,^[104] which could be further increased to 143 mAh g^{-1} through the optimization of electrolytes.^[105] Later, modified PANI,^[106-109, 111] PANI/TiO₂ and PANI/graphite composite^[110, 112] based Zn batteries delivered clearly enhanced capacity storage and cycling stability.

More recently, Chen et al. proposed the observation of a dual-ion mechanism on PANI **1**.^[113] The synthesized PANI **1** on carbon felts show homogeneously-distributed nanothorn structure, which could be beneficial to the diffusion kinetics upon charge storage. The half-doped PANI **1** was able to accept and release cations and anions (Zn^{2+} and CF_3SO_3^-) simultaneously. Due to such a superiority, the PANI/Zn cell delivered a high capacity of 200 mAh g^{-1} with an average output voltage of 1.1 V . Additionally, benefiting from the excellent Zn plating and stripping behavior in the aqueous $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ electrolyte, no obvious dendrites could be observed from the surface of Zn after a long-term cycling up to 3000 times (Figure 6a). Owing to the good cell performance, flexible and wearable PANI/Zn batteries with stable performance were further developed by using gel electrolytes (Figure 6b-c). Furthermore, Sun et al. reported the synthesis of sulfo self-doped PANI **1** (PANI-S) nanorods

with diameter and length of about 50 and 200 nm through the facile electrochemical copolymerization.^[114] As supported by X-ray photoelectron spectroscopy (XPS) characterization, PANI-S showed the ability to work as an organic reservoir to store multiple ions, not only limited to the electrolyte species such as SO_4^{2-} and Zn^{2+} , but also protons (H^+) (Figure 6d). As a result of this unique mechanism, the self-doped PANI-S/Zn cell produced a capacity of 184 mAh g^{-1} at 0.2 A g^{-1} . A high capacity of 110 mAh g^{-1} was still maintained at 10 A g^{-1} after 2000 cycles (Figure 6e-f). On the contrary, the non-doped PANI suffered from the sharp capacity fading during the cycling. All these studies as well as optimization works showed the great potential of conductive polymers as promising cathodes for rechargeable Zn batteries.

Radical polymers are well known for their rapid redox process, allowing the development of ultrafast charge-discharge organic batteries. As shown in Figure 7a, the as-obtained nitroxide radical polymer poly(2,2,6,6-tetra-methylpiperidinyloxy-4-yl vinyl ether) (PTVE) **19** delivered an initial capacity of 131 mAh g^{-1} with a retention of 75% after 1000 cycles through a three-electrode setup.^[28] To be highlighted that, the cell survived at a variety of current rates ranged from 60-1200 C. Even under an ultrahigh rate of 1200 C (corresponding to a charging of only 3 seconds), a large capacity of 127 mAh g^{-1} could still be achieved. When further fabricated with a Zn anode, the two-electrode aqueous PTVE/Zn cell gave a high output voltage of 1.7 V at 60 C, with a capacity retention of more than 65% after 500 cycles (Figure 7b).^[29] Apart from radical polymers, a redox-active polymer poly(vinylTTF) **20** with a conjugated backbone was also observed to have excellent rate capability.^[115] The aqueous poly(vinylTTF)/Zn cell with a loading of 20 wt% poly(vinylTTF) delivered a capacity of 111 mAh g^{-1} . A high capacity retention of 96% was maintained after 1000 cycles (Figure 7c). Remarkably, even when increasing the active material loading of poly(vinylTTF) to 50 wt%, the cell could last for 10000 cycles with negligible capacity fading at various current rates (from 10 C to 120 C) (Figure 7d). Although these two p-type polymers showed fast

charge-discharge stability, the limited electrons (usually one-electron-transfer) involved in the redox reactions reduce the storage ability of organic materials. Therefore, further developments of organic electrodes with higher capacity storage are essentially desirable. Especially, through the designing and tailoring of n-type organic compounds with multiple redox centers, higher energy storage organic-based rechargeable Zn batteries can be obtained. For this reason, multi-carbonyl-containing compounds can become a smart choice.

A series of quinone compounds in different positions were investigated as the cathode materials in a recent study.^[116] The selected compounds: 1,2-naphthoquinone (1,2-NQ) **21**, 1,4-naphthoquinone (1,4-NQ) **22**, 9,10-anthraquinone (9,10-AQ) **23**, 9,10-phenanthrenequinone (9,10-PQ) **24** and calix[4]quinone (C4Q) **25** showed feasible Zn^{2+} uptake characteristics. Among them, 1,4-NQ **22**, 9,10-AQ **23**, and C4Q **25** with carbonyls in para-position delivered enhanced electrochemical performance than those (1,2-NQ **21** and 9,10-PQ **24**) with carbonyls in ortho-position. This was explained by the larger steric hindrance of ortho-carbonyls as compared with para-carbonyls for Zn^{2+} insertion. It is worth highlighting that C4Q **25** showed the highest Zn^{2+} storage (335 mAh g⁻¹, corresponding to three Zn^{2+} per molecule) among those compounds, with a flat operating voltage of 1.0 V and an ultra-low polarization (Figure 8a). Moreover, the structural evolution of C4Q **25** upon Zn^{2+} insertion was confirmed by in-situ and operando characterizations, and the aqueous C4Q/Zn cell sustained a high capacity retention of 87% after 1000 cycles (Figure 8b). This in-depth study suggests the potential of carbonyl compounds, especially quinones to serve as higher Zn^{2+} storage organic materials as compared with those electrodes made from conductive and radical polymers. Moreover, the as-observed polarization voltage of quinones is comparable or even better than radical polymers. Since then, quinone compounds have gained increasing research interest for rechargeable Zn batteries. As a high capacity and long-lasting polyquinone electrode, poly(benzoquinonylsulfide) (PBQS) **26**, which has been previously developed for non-aqueous rechargeable Li and Na batteries,^[117] was also investigated in an

aqueous Zn battery.^[118] The as-prepared PBQS **26** was obtained in bulk form with micro-sized blocks. Based on the two active carbonyl groups, the PBQS/Zn cell delivered an initial Zn^{2+} storage of 203 mAh g⁻¹ (at 0.1 C), and a capacity retention of 86% was still maintained after 50 cycles at 0.2 C (Figure 8c).

To further enhance the Zn^{2+} storage ability of organic materials, an innovative Zn-ion coordination strategy was proposed by employing PTO **27** as the cathode.^[72] Interestingly, contrary to the observation on 9,10-PQ,^[116] which could only achieve half of its theoretical capacity (indicating the utilization of only one carbonyl group) due to the steric hindrance of the adjacent carbonyl groups, the as-prepared PTO **27** could achieve full utilization of its all four carbonyl groups (a two- Zn^{2+} reaction per formula unit) (Figure 8d). Among those, one Zn ion was coordinated with the two adjacent carbonyl groups in the ortho-position. Another Zn ion was accommodated by two PTO **27** molecules through the coordination of the remaining two carbonyl groups. The as-obtained PTO **27** nanorods exhibited inherent insolubility in an aqueous 2 M ZnSO_4 electrolyte, showing an extraordinary high capacity of 336 mAh g⁻¹ at 0.04 A g⁻¹. More importantly, excellent cycling and rate stability were obtained from both the coin and flexible belt-shaped PTO/Zn batteries.

Since most of organic electrode materials, particularly polymers, are in their amorphous states and do not show good crystallinity, the structural change of organic crystals upon Zn^{2+} insertion become a challenging topic. Recently, the phase transformation of an organic crystal tetrachloro-1,4-benzoquinone (p-chloranil) **28** was investigated.^[73] Pristine p-chloranil **28** initially formed a film (Figure 8e) by coating onto the mesoporous carbon additives through a nanoconfinement strategy, which could afford improved electrochemical performance. Interestingly, upon discharging, its morphology converted into rod-shaped fibers (Figure 8f), which did not change back to the film-like coating but transformed into rhombus particles (Figure 8g). Such an unusual morphology evolution was explained by a water-assisted phase transformation process, wherein one Zn^{2+} was inserted between two p-chloranil molecules,

delivering a maximum Zn^{2+} storage of 205 mAh g^{-1} at 1.1 V with a moderate capacity retention after 200 cycles.

5. Organic Electrodes for Rechargeable Ca and Ca-Ion Batteries

Calcium is the 3rd most abundant metal element in Earth's crust and possesses an attractive theoretical gravimetric capacity of 1337 mAh g^{-1} . As a reactive divalent candidate, it belongs to the group of alkaline earth metals. The standard redox potential of Ca/Ca^{2+} (-2.87 V vs. NHE) is close to that of Li/Li^+ (-3.04 V vs. NHE), and much wider than Mg/Mg^{2+} (-2.37 V vs. NHE) and Zn/Zn^{2+} (-0.76 V vs. NHE), endowing organic-based rechargeable Ca batteries with a potential higher energy density compared with those of rechargeable Mg and Zn batteries. Pioneering study by Aurbach et al. indicated that Ca metal anodes could impossibly be reversibly plated and stripped in conventional organic electrolyte systems.^[119] Therefore, rechargeable Ca batteries have not been taken seriously for a long time, though the exploration on Ca^{2+} host materials has never stopped. Only in 2015, it was first observed that Ca could undergo a reversible plating and stripping in conventional aprotic electrolytes,^[120] nevertheless, a moderate high temperature up to 75 $^{\circ}\text{C}$ was required to make the process happen (Figure 9a). Very recently, Ca plating and stripping has been successfully demonstrated in an organic electrolyte ($\text{Ca}(\text{BH}_4)_2$ in THF) at room temperature with the improved reversibility and CE (Figure 9b).^[121] This study reveals the possibility of future practical application of Ca metal based rechargeable batteries.

Although several materials have been reported to store Ca^{2+} successfully,^[11] until now, very few investigations on organic materials have been conducted.^[83, 122] One of the examples was from PTCDA **12**.^[83] Inspired by its reversible Mg^{2+} storage ability, the Ca^{2+} storage ability of PTCDA was also checked. The aqueous full-cell assembled with submicron PTCDA rod anode and activated carbon cathode showed an initial capacity of 87 mAh g^{-1} . However, a

rapid declination was found from the cycling (Figure 9c). Another example was from the frequently investigated polyimide compound **14** (named poly[N,N-(ethane-1,2-diyl)-1,4,5,8-naphthalenetetracarboxiimide] (PNDIE) in the article).^[122] The as-synthesized PNDIE **14** powders were aggregated particles with diameters of less than 1 μm . PNDIE **14** in a typical three-electrode configuration delivered a capacity approximate to 148 mAh g^{-1} (Figure 9d), and the cell achieved a capacity retention of 80% even after 4000 cycles (Figure 9e). Furthermore, coupled with a copper hexacyanoferrate (CuHCF) cathode (Figure 9f), the aqueous PNDIE/CuHCF full-cell also showed an excellent cycling stability. Although the shuttling Ca^{2+} ions in above-mentioned two examples were purely contributed by the electrolytes (since the counter electrodes used were not Ca metals), the results suggest the possibility of organic compounds as effective host materials for Ca^{2+} storage. By reviewing the progress and current situation of organic compounds on rechargeable Ca batteries, there is still a long way to go. Moreover, the selection and modification of Ca^{2+} containing electrolyte systems are essentially critical. There is still a plenty of room to optimize the electrochemical performance of organic electrodes with appropriate solvents and Ca salts.

6. Organic Electrodes for Rechargeable Al & Al-Ion Batteries

As the most abundant metal element in Earth's crust, aluminum with a high gravimetric capacity of 2980 mAh g^{-1} , is a promising safe electrode candidate for next-generation of rechargeable batteries. The concept of organic materials as electrodes for rechargeable Al batteries has been proposed for more than 30 years. Literature studies have already confirmed the electrochemical deposition and stripping of Al metal in Al-based ionic liquid electrolytes.^[123-126] Almost during the same period, demonstrations have shown that conductive polymers including PPy,^[127-128] PTh,^[129] PANI^[130-131] and Poly(p-phenylene) (PPP)^[132-133] could undergo electrochemical reactions in Al-based electrolytes. However, such

preliminary results mainly came from cyclic voltammetry studies. In addition, very limited battery-relevant demonstrations have been conducted. For this reason, research on rechargeable Al batteries has shifted from conductive polymers to graphite and inorganic materials.^[134-140] Due to the strong coordination ability of trivalent Al-ions (Al^{3+}) with electrolyte species, state-of-the-art demonstrations on active cathode materials mainly rely on the insertion of AlCl_4^- . By deploying the widely-used mixture electrolyte AlCl_3 /1-ethyl-3-methylimidazolium chloride ($[\text{EMIm}]\text{Cl}$),^[126] AlCl_4^- and Al_2Cl_7^- redox anions could be produced, allowing the occurrence of anion insertion/deinsertion at the cathode and Al plating/stripping at the anode (Figure 10a).^[134]

As for organic compounds, only recently, the chloroaluminate-doped PPy **29** and undoped PTh **30** have been demonstrated to deliver improved battery performance.^[141] The assembled doped-PPy/Al and PTh/Al cells delivered an initial capacity of around 72 and 88 mAh g^{-1} , respectively. Although capacity declination could still be observed from the cycling performance of both compounds (Figure 10b-c), this study successfully evaluated the electrochemical reversibility of conductive polymers versus Al anodes. More recently, pyrene **31** and its conjugated polymer derivatives (polypyrene **32**, and poly(nitropyrene-co-pyrene) **33**) have been investigated with respect to the insertion of AlCl_4^- .^[142] Among those compounds, monomeric pyrene **31** could only accept a limited amount of AlCl_4^- due to the tight packing of molecules in its crystalline form (Figure 10d, left). On the contrary, polypyrene **32** with an amorphous structure showed a much improved AlCl_4^- insertion ability (Figure 10d, right), providing a stable capacity of 70 mAh g^{-1} after 300 cycles. Moreover, poly(nitropyrene-co-pyrene) **33** with a modified structure delivered an output voltage of 1.7 V (vs. Al/Al^{3+}) along with an average capacity of 100 mAh g^{-1} for 1000 cycles (Figure 10e).

Since the ions stored by organic cathode materials in Al batteries are dominantly negatively-charged AlCl_4^- anions, carbonyl compounds that based on the insertion of positively-charged metal cations do not seem to be suitable for rechargeable Al batteries.

Nevertheless, there was an Al battery demonstration on carbonyl compound as the cathode. As previously mentioned in the rechargeable Mg battery section, the PI@CNT **15** microparticles obtained by Wang et al. has also been fabricated into an rechargeable Al battery.^[21] The PI@CNT/Al cell delivered a high capacity of 110 mAh g⁻¹ after 100 cycles. Although the redox mechanism of such an Al battery was unclear, this study first revealed the opportunity of a carbonyl compound as an effective electrode for Al batteries. More recently, a unique charge storage route through positively-charged AlCl₂⁺ insertion was observed on a series of redox-active phenanthrenequinone (PQ)-based organic compounds: PQ monomer (PQ-Ref) **34**, linear PQ trimer (PQ-Lin) **35** and triangular phenanthrenequinone-based macrocycle PQ-Δ **36**.^[143] The two adjacent carbonyl groups attached onto the phenanthrene backbones allow the formation of tetracoordinate organic complexes^[144-145] (e.g. Figure 11a, taken (PQ-Δ^{3*})• 3AlCl₂ as an example) upon discharging in AlCl₃/[EMIm]Cl electrolyte. Based on this novel mechanism, a long-lasting Al battery with stable cycling and excellent reversibility was achieved on microstructured PQ-Δ **36** (Figure 11b). This study proposes a potential direction for organic based Al batteries. With further investigations, more carbonyl compounds are expected to be developed for future organic electrode based rechargeable Al batteries.

7. Conclusion

In this review, to the best of our knowledge, we have summarized the recently-reported organic materials for promising multivalent metal and metal-ion rechargeable batteries. Starting from the early demonstrations on conductive polymers, organic materials including organosulfurs, nitroxide radicals and carbonyl-containing compounds have been investigated for more than 30 years versus multivalent metals (Mg, Zn, Ca & Al). However, compared with the investigations on inorganic materials at that period, much less attention has been paid

to organic compounds for their poor charge-discharge reversibility and limited cycling stability. Only recently, with the selection and exploration of suitable electrolyte systems, either aqueous or nonaqueous, the electrochemical performance of organic materials has been greatly improved versus multivalent metals. With the innovation in designing and tailoring, the advantages of organic materials, for example, the high operating voltage of conductive polymers, the rapid redox process of nitroxide radicals, and the large capacity storage of carbonyl compounds have been clearly confirmed versus multivalent metals.

Nevertheless, the evaluations on organic-based multivalent metal-ion rechargeable batteries are still not enough. Difficulties and shortcomings are clearly present for each system. For example, the sluggish reaction kinetics as well as the lack of detailed characterizations to identify the real insertion mechanisms (whether based on Mg^{2+} , Mg_xCl_y^+ or other types of solvated ions) in organic based Mg batteries. Although aqueous electrolyte based organic rechargeable Zn batteries show good safety and ultra-long stability, the relatively low average output voltage (normally <1.2 V) limits their applications for high-energy purposes. As for organic-based rechargeable Ca batteries, the research progress is still in its infancy. More efforts are required to explore proper calcium salts and solvents, enabling the reversible plating and stripping of Ca metals with high efficiency at room temperature. As previously mentioned, the transition of insertion chemistry from p-type AlCl_4^- to n-type AlCl_2^+ on organic compounds offers chemists confidence to search for advanced Al batteries. However, the number of electron (one-electron) involved in the redox reaction is still not enough. With further exploration of proper electrolyte solutions and structural tailoring of organic electrode materials, organic-based batteries based on complete trivalent Al^{3+} (three-electron) storage are to be developed.^[146] Despite the accomplishments achieved by organic materials thus far, general challenges associated with the moderate reversibility, low output voltage, and large polarization for multivalent metal and metal-ion rechargeable batteries are needed to be solved in future. Apparently, in-depth understanding of the detailed charge-

storage mechanisms in aforementioned organic materials with regard to different multivalent metals remains limited. Moreover, learning from the successful experience of organic based rechargeable Li batteries, careful morphology modification through nanotechnology might be helpful to obtain organic nanostructures with improved electrochemical performance and enhanced flexibility. These recommendations are critical toward developing high-performance organic-based multivalent metal and metal-ion rechargeable batteries. Anyhow, there is still a long way to go to achieve more advancement in this field.

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Figure 1. (a) Charge and discharge profiles (the 1st and 10th cycle) of DMcT-PANI/Mg cell. (b) Cycling performance of DMcT-PANI/Mg cell. (c) Cycling performance of PDTDA/Mg cell (inset shows the initial charge and discharge profiles). (d) Cycling performance (discharge capacity vs. cycle) of carbyne polysulfide/Mg cell at a small current density of 5.4 mA g⁻¹. Reproduced with permission.^[25] Copyright 2007, Elsevier. Reproduced with permission.^[70] Copyright 2014, Hindawi Publishing Corporation.

Figure 2. (a) Illustration of the configuration of PTMA/Mg cell. (b) Charge and discharge profiles of PTMA/Mg cell (only one cycle was obtained due to the dissolution issue). (c) Initial charge and discharge profiles of DMBQ/Mg cell with 0.5 M Mg(ClO₄)₂/γ-butyrolactone. (d) Charge and discharge profiles (the 1st and 10th cycle) of DMBQ/Mg cell with 0.5 M Mg(TFSI)₂ in sulfolane. Charge and discharge profiles (e) and (f) Cycling performance of DMBQ/Mg cell with 0.5 M Mg(TFSI)₂-2MgCl₂ in DME. Reproduced with permission.^[27] Copyright 2014, American Chemical Society. Reproduced with permission.^[30] Copyright 2012, The Chemical Society of Japan. Reproduced with permission.^[31] Copyright 2014, The Electrochemical Society. Reproduced with permission.^[76] Copyright 2016, The Electrochemical Society.

Figure 3. (a) Charge and discharge profiles (the initial 5 cycles) of PAQS/Mg powder cell. Inset shows the cycling performance of this cell. (b) Cycling performance of 14PAQ/Mg cell. (c) Charge and discharge profiles of 14PAQ/Mg cell at different cycles with a small polarization effect. (d) Electrochemical performance of PHBQS/Mg cell (inset shows the charge and discharge profiles at different cycles). (e) Potential versus capacity chart of several representative small molecules with high storage. (f) Cycling performance of PPTO/Mg cell. (g) The initial crystal structure (left) and the crystal structure after Mg^{2+} insertion (right) of PTCDA. (h) Rate performance represented by the charge and discharge profiles of PTCDA upon the insertion of Mg^{2+} . Reproduced with permission.^[77] Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.^[78] Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.^[81] Copyright 2016, Elsevier. Reproduced with permission.^[20] Copyright 2017, Springer Nature. Reproduced with permission.^[83] Copyright 2017, American Chemical Society.

Figure 4. (a) Cycling performance of polyimide/Mg cell. (b) Scanning electron microscopy (SEM) image and fourier-transform infrared spectroscopy (FTIR) of PPMDA@MCNTs composite. (c) Cycling performance of PPMDA@MCNTs composite when fabricated into a three-electrode cell. (d) Demonstration of a dual-ion all-organic-electrode cell based on PDI-EDA anode and PTPAn cathode. (e) Cycling performance of the PDI-EDA/PTPAn dual-ion cell. (f) Layered crystal structure of sodium rhodizonate (Na₂C₆O₆). (g) Schematic illustration of an artificial interphase coated onto Mg powder electrode made from cPAN and Mg triflate (left) and the proposed structure of the interphase (right). Reproduced with permission.^[79] Copyright 2017, American Chemical Society. Reproduced with permission.^[89] Copyright 2017, American Chemical Society. Reproduced with permission.^[91] Copyright 2018, The Royal Society of Chemistry. Reproduced with permission.^[97] Copyright 2018, American Chemical Society. Reproduced with permission.^[98] Copyright 2018, Springer Nature.

Figure 5. Reaction mechanisms and schematic illustrations of organic materials in (a) chloride-containing and (b) chloride-free electrolytes. (c) Cycling stability and (d) rate profiles of P(NDI2OD-T2) in chloride-free electrolyte. Reproduced with permission.^[99] Copyright 2018, Elsevier.

Figure 6. (a) Cycling performance of half-doped PANI/Zn cell. (b) Schematic illustration of a flexible and wearable PANI/Zn battery. (c) Digital image of the LED array powered by the PANI/Zn battery. (d) Proposed mechanism and structures of PANI-S upon charging (oxidation) and discharging (reduction) versus Zn metal. (e) Charge and discharge profiles of PANI-S/Zn cell at different current densities. (f) Cycling performance of PANI-S/Zn cell. Reproduced with permission.^[113] Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.^[114] Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA.

Figure 7. (a) Electrochemical performance of PTVE based three-electrode cell. (b) Electrochemical performance of PTVE/Zn cell. (c) Cycling performance and rate profiles of poly(vinylexTTF)/Zn cell with a loading of 20 wt% poly(vinylexTTF). (d) Rate performance of poly(vinylexTTF)/Zn cell with a loading of 50 wt% poly(vinylexTTF). Reproduced with permission.^[28] Copyright 2009, The Royal Society of Chemistry. Reproduced with permission.^[29] Copyright 2009, Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.^[115] Copyright 2016, Springer Nature.

Figure 8. (a) Charge and discharge profiles (the initial 5 cycles) of C4Q/Zn cell with a low polarization of 70 mV. (b) Cycling performance of C4Q/Zn cell at 500 mA g^{-1} . (c) Cycling performance of PBQS/Zn cell. (d) Schematic illustration and mechanism of an environmentally friendly PTO/Zn cell. SEM characterization of p-chloranil electrode at the (e) Pristine (f) discharged and (g) charged states. Reproduced with permission.^[116] Copyright 2018, American Association for the Advancement of Science. Reproduced with permission.^[118] Copyright 2018, The Royal Society of Chemistry. Reproduced with permission.^[72] Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.^[73] Copyright 2018, American Chemical Society.

Figure 9. (a) Cyclic voltammograms indicating the reversible Ca plating and stripping process at the temperature of 75 and 100 °C. (b) Galvanostatic study of the reversible plating and stripping of Ca at room temperature (inset shows the CE versus cycle number). (c) Charge and discharge profiles (the initial 10 cycles) of PTCDA/activated carbon cell. (d) Initial charge and discharge profiles (I-initial state, II-discharged state, III-Charged state) of PNDIE in a three-electrode cell. (e) Schematic illustration of a PNDIE/CuHCF full-cell. Reproduced with permission.^[120] Copyright 2015, Springer Nature. Reproduced with permission.^[121] Copyright 2017, Springer Nature. Reproduced with permission.^[83] Copyright 2017, American Chemical Society. Reproduced with permission.^[122] Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA.

Figure 10. (a) Schematic illustration and mechanism explanation of an Al rechargeable battery based on Al anode and graphite cathode in an $\text{AlCl}_3/[\text{EMIm}]\text{Cl}$ ionic liquid electrolyte. (b) Charge and discharge profiles of PPy (top) and PTh (bottom). The 5th (solid line) and 100th (dashed line) are presented. (c) Cycling performance of PPy (top) and PTh (bottom). (d) Schematic illustration of the structure and insertion difference between pyrene and polypyrene. Reproduced with permission.^[134] Copyright 2015, Springer Nature. Reproduced with permission.^[141] Copyright 2014, American Chemical Society. Reproduced with permission.^[142] Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA.

Figure 11. (a) Structure and redox mechanism of PQ- Δ upon discharge and charge. (b) Long-term cycling of PQ- Δ versus Al metal at $2\ A\ g^{-1}$. Reproduced with permission.^[143] Copyright 2018, Springer Nature.

Table 1. Summary of organic compounds as effective electrodes for multivalent metal (Mg, Zn, Ca & Al) rechargeable batteries.

Compound ^[ref]	Structure	Counter electrode	Insertion ion & type ^{a)}	Electrolyte	Voltage window (V)	Initial reversible capacity (mAh g ⁻¹) at current density (mA g ⁻¹) ¹⁾	Cyclability (mAh g ⁻¹), current density (mA g ⁻¹)
1 ^[24, 113-114] PANI		Mg	Cl ⁻ ; Br ⁻ ; ClO ₄ ⁻ p-type	2 M MgCl ₂ ; MgBr ₂ ; Mg(ClO ₄) ₂ (aqueous)	1.0-1.6	- ^{b)}	-
		Zn	CF ₃ SO ₃ ⁻ p-type	1 M Zn(CF ₃ SO ₃) ₂ (aqueous)	0.5-1.5	200 at 50; ~89 at 5000	82 after 3000 cycles, 5000
		Zn	SO ₄ ²⁻ p-type	1 M ZnSO ₄ (aqueous)	0.5-1.6	184 at 20; ~100 at 10000	110 after 2000 cycles, 10000
2 ^[25] DMcT		Mg	Mg ²⁺ n-type	0.25 M Mg(AlCl ₂ BuEt) ₂ /THF	0.3-2.0	16.8 at 25	27.2 after 26 cycles, 25
3 ^[25] PTTDA		Mg	Mg ²⁺ n-type	0.25 M MgAlCl ₃ Bu ₂ /THF	0.3-1.8	~50 at 25	~65 after 33 cycles, 25
		Mg	Mg ²⁺ n-type	0.25 M Mg(AlCl ₂ BuEt) ₂ /THF	0.3-2.0	117.3 at 25	~73 after 22 cycles, 25
4 ^[25] CSM		Mg	Mg ²⁺ n-type	0.25 M Mg(AlCl ₂ BuEt) ₂ /THF	0.3-2.0	117.3 at 25	~73 after 22 cycles, 25
5 ^[26-27] PTMA		Mg	Mg ²⁺ n-type	0.25 M Mg(AlCl ₂ BuEt) ₂ /THF	0.3-1.8	81.2 at 22.8	~23 after 21 cycles, 22.8
		Mg	TFSI ⁻ p-type	0.3 M Mg(TFSI) ₂ in glyme/diglyme	1.75-3.4	37.6 at 0.02 C	-
6 ^[30-31, 76] DMBQ		Mg	Mg ²⁺ n-type	0.5 M Mg(ClO ₄) ₂ /butyrolactone	0.2-1.6	260 at 20	~221 after 5 cycles, 20
		Mg	Mg ²⁺ n-type	0.5M Mg(TFSI) ₂ in sulfone-based solvents	0.0-4.0	~50 at 10	~20 after 100 cycles, 10
		Mg	Mg ²⁺ n-type	0.5 M Mg(TFSI) ₂ -2MgCl ₂ in DME	0.5-2.8	226 at 0.2 C	74 after 30 cycles, 0.2 C

7 ^[77] PAQS		Mg	Mg ²⁺ n-type	0.37 M MgCl ₂ and 0.15 M Mg(TFSI) ₂ in THF/glyme	0.5-2.5	225 at 50	~60 after 100 cycles, 50
		Mg	Mg ²⁺ n-type	0.3 M Mg(HMDS) ₂ - 4MgCl ₂ /THF	0.5-2.5	100 at 112	~30 after 100 cycles, 112
8 ^[78] 14PAQ		Mg	Mg ²⁺ n-type	0.3 M Mg(HMDS) ₂ - 4MgCl ₂ /THF	0.5-2.5	122 at 130	100.2 after 100 cycles, 130
9 ^[78] 26PAQ		Mg	Mg ²⁺ n-type	0.3 M Mg(HMDS) ₂ - 4MgCl ₂ /THF	0.5-2.5	132.7 at 130	104.9 after 100 cycles, 130
10 ^[81] PHBQS		Mg	Mg ²⁺ n-type	0.48 M MgCl ₂ and 0.32 M Mg(TFSI) ₂ in tetraglyme and 1,3- dioxolane	0.8-3.0	~75 at 50	~140 after 25 cycles, 50
11 ^[20] PPTO		Mg _x Cu _{1-x} HC F	Mg ²⁺ n-type	4.5 M Mg(NO ₃) ₂ (aqueous)	0.3-1.1	144 at 70	95 after 1000 cycles, 70
12 ^[83] PTCDA		Activated carbon	Mg ²⁺ n-type	4.8 M Mg(NO ₃) ₂ (aqueous)	-0.8-0.2 (vs. Ag/AgCl)	136 at 500	~80 after 37 cycles, 20- 500
		Activated carbon	Ca ²⁺ n-type	Saturated Ca(NO ₃) ₂ (aqueous)	0.0-1.5	87 at 20	61 after 10 cycles, 20
13 ^[90] NP		Mg with 5% wt% MgCl ₂	Mg ²⁺ n-type	0.4 M Mg(TFSI) ₂ & 0.4 M MgCl ₂ in tetraglyme/D ME/1,3- dioxolane	0.8-2.5	45 at 50	85 after 100 cycles, 50
14 ^[79, 122] Polyimide or PNDIE		Activated carbon	Mg ²⁺ n-type	1M MgSO ₄ (aqueous)	-0.8-0.0 (vs. Ag/AgCl)	140 at 1000	126 after 2000 cycles, 1000
		Nickel hexacyano ferrate	Mg ²⁺ n-type	1M MgSO ₄ (aqueous)	0.0-1.55	33 at 2000	20 after 5000 cycles, 2000
		Activated carbon	Ca ²⁺ n-type	2.5 M Ca(NO ₃) ₂ (aqueous)	-0.9-0.0 (vs. Ag/AgCl)	160 at 37; 130 at 925	105 after 4000 cycles, 925
		Ca _{0.3} CuH CF	Ca ²⁺ n-type	2.5 M Ca(NO ₃) ₂	0.5-1.9	~27 at 400	~24 after 1000 cycles

(aqueous)							
15 ^[21, 89] PPMDA or PI		Activated carbon LVP Mg Al	Mg ²⁺ n-type Mg ²⁺ n-type -	4 M Mg(TFSI) ₂ (aqueous) 4 M Mg(TFSI) ₂ (aqueous) Phenyl magnesium chloride (PhMgCl) and AlCl ₃ /THF AlCl ₃ /[EMIm] JCl	1.7-2.5 (vs. Mg/Mg ²⁺) 0.4-1.9 0.6-2.2 0.2-1.1	110 at 100 42 at 2000 ~140 at 150 ~137 at 150	96 after 500 cycles, 100 39 after 6000 cycles, 2000 ~130 after 200 cycles, 150 ~110 after 100 cycles, 150
16 ^[91] PDI-EDA		PTPAn	Mg ²⁺ n-type	Anhydrous Mg(ClO ₄) ₂ /A cetonitrile	0.01-1.6	90 at 50; 64.9 at 1000	74.1 after 2000 cycles, 1000
17 ^[97] Na ₂ C ₆ O ₆		Mg	Li ⁺ & Mg ²⁺ n-type	0.25 M all- phenyl complex (APC) and 1 M LiCl/THF	0.1-2.75	350 at 50	~200 after 50 cycles, 50
18 ^[99] P(NDI2OD-T2)		Mg	MgCl ⁺ & Mg ²⁺ n-type	0.2M Mg(TFSI) ₂ in diglyme	0.8-2.0	49 at 300	43 after 2500 cycles, 300
19 ^[28-29] PTVE		Pt Zn	Cl ⁻ p-type Cl ⁻ p-type	0.1 M NaCl (aqueous) 0.1 M ZnCl ₂ and 0.1M NH ₄ Cl (aqueous)	0.4-1.0 1.4-2.0	131 at 60 C 124 at 60 C	~98 after 1000 cycles, 60 C ~81 after 500 cycles, 60 C
20 ^[115] Poly(vinylexT TF)		Zn	BF ₄ ⁻ p-type	1 M Zn(BF ₄) ₂ hexahydrate (aqueous)	0.6-1.7	128 at 20 C; 110 at 120 C; 100 at 10 C	111 after 1000 cycles, 120 C; 81 after 10000 cycles, 10- 120 C
21 ^[116] 1,2-NQ		Zn	Zn ²⁺ n-type	3 M Zn(CF ₃ SO ₃) ₂ (aqueous)	0.5-1.8	68 at 20	~55 after 5 cycles
22 ^[116] 1,4-NQ		Zn	Zn ²⁺ n-type	3 M Zn(CF ₃ SO ₃) ₂ (aqueous)	0.2-1.7	149 at 20	~46 after 5 cycles

23 ^[116] 9,10-AQ		Zn	Zn ²⁺ n-type	3 M Zn(CF ₃ SO ₃) ₂ (aqueous)	0.2-1.8	194 at 20	~124 after 40 cycles
24 ^[116] 9,10-PQ		Zn	Zn ²⁺ n-type	3 M Zn(CF ₃ SO ₃) ₂ (aqueous)	0.2-1.8	111 at 20	~88 after 5 cycles
25 ^[116] C4Q		Zn	Zn ²⁺ n-type	3 M Zn(CF ₃ SO ₃) ₂ (aqueous)	0.2-1.8	335 at 20; ~140 at 500	~122 after 1000 cycles, 500
26 ^[118] PBQS		Zn	Zn ²⁺ n-type	3 M Zn(CF ₃ SO ₃) ₂ (aqueous)	0.2-1.8	203 at 0.1 C; 108 at 0.2 C	150 after 50 cycles, 0.2 C
27 ^[72] PTO		Zn	Zn ²⁺ n-type	2 M ZnSO ₄ (aqueous)	0.36-1.46	336 at 40; ~207 at 3000	145 after 1000 cycles, 3000
28 ^[73] p-chlorani		Zn	Zn ²⁺ n-type	1 M Zn(CF ₃ SO ₃) ₂ (aqueous)	0.8-1.4	170 at 0.2 C; 118 at 1 C	90 after 100 cycles, 0.2 C; 83 after 200 cycles, 0.2 C
29 ^[141] PPy		Al	AlCl ₄ ⁻ p-type	AlCl ₃ /[EMIm] JCl	0.8-2.0	~72 at 20	48 after 100 cycles, 20
30 ^[142] PTh		Al	AlCl ₄ ⁻ p-type	AlCl ₃ /[EMIm] JCl	0.8-2.0	~88 at 16	70 after 100 cycles, 16
31 ^[142] Pyrene		Al	AlCl ₄ ⁻ p-type	AlCl ₃ /[EMIm] JCl	1.05-2.2	20 at 200	~10 after 300 cycles, 200
32 ^[142] Polypyrene		Al	AlCl ₄ ⁻ p-type	AlCl ₃ /[EMIm] JCl	1.05-2.2	~92 at 200	~70 after 300 cycles, 200
33 ^[142] Poly(nitropyrene-co-pyrene)		Al	AlCl ₄ ⁻ p-type	AlCl ₃ /[EMIm] JCl	1.05-2.2	~162 at 200	~86 after 1000 cycles, 200
34 ^[143] PQ-Ref		Al	AlCl ₂ ⁺ n-type	AlCl ₃ /[EMIm] AlCl ₄	0.8-1.75	~27 at 200	17 after 200 cycles, 200
35 ^[143] PQ-Lin		Al	AlCl ₂ ⁺ n-type	AlCl ₃ /[EMIm] AlCl ₄	0.8-1.75	~51 at 200	13 after 200 cycles, 200

36 ^[143]	Al	AlCl ₂ ⁺	AlCl ₃ /[EMIm AlCl ₄]	0.8-1.75	~80 at 200 ^{c)} ;	82 after 200 cycles, 200;
PQ-Δ		n-type			~90 at 2000	53 after 5000 cycles, 2000

^{a)}The type of ion insertion is based on the ions inserted into the organic host materials.

^{b)}Not applicable. The values are not able to be obtained or estimated from the reference studies.

^{c)}The initial capacity is subject to different degrees of activation.

Author biographies:

Dr. Jian Xie received his B. Eng. and Ph. D degrees in Materials Science and Engineering (MSE) from Nanyang Technological University (NTU). He is a research fellow in Prof. Qichun Zhang's group, NTU, Singapore. He currently focuses on the development of organic electrode materials for rechargeable lithium batteries and multivalent metal based rechargeable batteries.

Dr. Qichun Zhang is an associate Professor at the School of Materials Science and Engineering and an adjunct associate professor in the Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences at Nanyang Technological University (NTU, Singapore). His research focuses on conjugated rich carbon materials and applications. Currently, he is an associate editor for J. Solid State Chemistry, an Advisory board member of Materials Chemistry Frontiers, and an Advisory board member of Inorganic Chemistry Frontiers. He is also a fellow of the Royal Society of Chemistry and a highly-cited researcher for 2018. He has published more than 305 papers and 4 patents (H-index: 63).

Organic multivalent metal and metal-ion rechargeable batteries are reviewed. Fundamentals including organic structures, cell configurations and key relevant electrochemical parameters are presented. This review provides a fundamental guidance for future development of organic multivalent metal-ion rechargeable batteries.

Organic electrodes, multivalent metals, multivalent metal-ions, rechargeable batteries, lithium batteries

*Jian Xie, Qichun Zhang**

Recent Progress in Multivalent Metal (Mg, Zn, Ca & Al) and Metal-Ion Rechargeable Batteries with Organic Materials as Promising Electrodes

ToC figure