Review

Debating the magnesium–selenium battery technology

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Abstract

Magnesium ion batteries (MIBs) have received tremendous research attention owing to their low cost, dendrite free electroplating, and high theoretical capacities compared with lithium ion batteries (LIBs). Despite these advantages, the launching of MIBs is hindered by sluggish kinetics of the magnesium ions inside the host cathodes. Recently, several magnesium–selenium batteries have been developed to achieve the fast kinetics of magnesium ions inside the selenium-based cathodes. Herein, we have critically reviewed the five-year advancements made in the field of selenium cathode design, selenium loadings, compatible organic and inorganic electrolytes, their resultant reversible capacities, working voltages, cycle life, and specific energies. Selected selenium-based cathodes were critically debated in terms of their electrochemical performance and challenges. At the end of this review article, several innovative directions are proposed to shed light on future research.

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1. Introduction

The growing energy demands with persistent improvement in substantial production of durable materials for energy storage have provided a model paradigm to new energy storage regime. The energy management system is struggling hard to address the most crucial global problems related with energy demand, climate change, and petroleum economies. The efficient batteries with various performance profiles are considered as the backbone of energy systems for delivering power to both small and large scale. The performance-based capabilities of various batteries included thermal stability; appropriate potential range, sufficient energy density, and current production enabled them to be employed in different application such as modern hybrid cars, busses, drones, and even hybrid ships. Furthermore, these are also extended to small applications such as wearable electronics, biomedical devices, and portable electronic devices. Although there are many issues need to be addressed regarding the cost, safety, cycle life and other performance factors. Up to now, lithium-ion batteries are considered as developed and commercialized energy storage systems in the present market with enormous research progress. Perhaps, few questionable aspects of Li-ion batteries i.e. scarcity of Li-element on earth and its cost, are main reasons to bring innovation in alternate electrode materials by energy storage researchers to conquer the increasing demands of energy through the immense developments in hybrid cars, and all plug-in vehicles and even huge demands of grid storage applications from solar energy harvesters [1-3].

Magnesium-ion batteries are one of the possible substitutes of Li-ion batteries, with huge interest for many scientists in recent years. Many aspects of Mg-ion technology including the high natural abundance of magnesium in earth’s crust, with a rough estimation of 100 times greater than lithium, in expensiveness for electrode processing with a high melting point as compared to lithium, and more stable than lithium. [4] The volumetric capacity of Mg-ion battery is 3833 mA
h cm$^{-3}$, which is higher than the Li-ion battery (2046 mA h cm$^{-3}$), and is attributed to the divalent nature of Mg-ion. The research development in Mg-ion batteries have not been so extensively approached compared with Li-ion batteries due to some hurdles, which obstructed the good performance and findings of suitable electrolytes that can facilitate the reversible transportation of Mg-ion from the Mg anode. [5] Unlike Li-ion batteries, where the surface conduction is good due to formation of polar solid electrolyte interface films on Li-metal surface; the magnesium metal anode is covered with a film during the charging/discharging processes, which basically block the further conduction of Mg$^{2+}$ ions. [6] Despite these obstacles, research on magnesium-ion batteries is increasing day by day as confirmed by the literature reviews [7-9]. Recently, several host materials such as transition metal oxides, metal sulfides, and activated carbons, have been extensively explored to accommodate the magnesium-ions [10]. Although there are several exciting reports, but unavailability of compatible magnesium electrolytes has restricted their electrochemical performance [11-14]. To overcome these issues alternative strategies such as magnesium–lithium (Mg–Li), magnesium–sodium (Mg–Na), and magnesium–zinc (Mg–Zn) hybrid ion batteries have also been explored, which displayed excellent specific capacities and cycle life [10]. The high electrochemical performance of hybrid ion batteries is attributed to the high ionic conductivity of electrolyte and dendrite free cycling of magnesium anode. Similarly, the element sulfur is also tried as a composite cathode (S/C) in magnesium ion electrolytes. However, the severe magnesium-sulfur polysulfide shuttling effect have appeared as a new grand challenge for magnesium–sulfur batteries [15]. The Mg–S polysulfide shuttle effect is mainly attributed to the high reactivity of element sulfur with magnesium electrolytes.

Compared with sulfur (S), the selenium (Se) element is less reactive, easily controllable, and possess high electrical conductivity (Se: $1 \times 10^{-3}$ S m$^{-1}$, S: $5 \times 10^{-28}$ S m$^{-1}$), thus is more efficient. Regardless of lower gravimetric capacity of Se (678 mA h g$^{-1}$) as compared to that of S (1675 mA h g$^{-1}$), the Se has good theoretical volumetric capacity (3268 mA h cm$^{-3}$), which is almost equal to the theoretical volumetric capacity of S (3467 mA h g$^{-1}$). [16] Thus, both elements may exhibit similar energy and power densities, which is highly desirable for portable electronic devices. Hence, it is predicted that Mg–Se battery can give better rate performance and higher capacity as compare to Mg–S battery system. Battery scientists have developed many materials based on Se and S to increase the performance, solid solution of Se/S, and are very prominent as cathode materials for various battery systems, due to their miscibility in each other to make Se$_n$S$_{8-n}$ and Se$_x$S$_{12-x}$ compounds [17,18].

Inspired from these exciting properties and advantages (of selenium), several selenium-carbon composite cathodes have been employed in magnesium ion systems. Literature review revealed that during past decade several successful attempts were made to synthesize the possible selenium-based cathodes, activated carbons with high selenium loadings, separators, and both organic and inorganic electrolytes for magnesium–selenium batteries, which exhibited different results including rate performance, cycle life, working potentials and energy densities. Despite these significant developments in Mg–Se batteries, there is no report that has summarized these results for early stage researchers. Recently, Eftekhar et al. [19] attempted to summarize selenium-based battery, however his focus was on Li or Na ion systems. Thus, an up to date review on magnesium-selenium batteries is still missing. To fulfill this research gap, herein we have critically reviewed the recent advances made in the field of Mg–Se batteries ranging from Se-based composites to electrolyte strategies, and possible challenges.

2. Working mechanism of Mg–Se battery

The working mechanism of Mg–Se battery is of great importance because it helps the researchers to understand the basic chemistry and nature of reactions. Karger et al. [20] attempted to explain the chemical reactions with the help of X-ray photoelectron spectroscopy (XPS), while using the SeCMK-3 cathode (Fig. 1(a–b)). Firstly, selenium cathode was charged and then discharged at the current density of 20mA g$^{-1}$ followed by characterizations. The XPS analysis of cathode surface revealed the presence of Se 3d$_{5/2}$ and 3d$_{3/2}$ peaks, which corresponds to metallic selenium of SeCMK-3 composite. With increasing the reaction kinetics (at about 1.2 V), the shifting of Se 3d$_{5/2}$ peak towards low binding energies indicates the formation of magnesium-selenium polyselenide, MgSe$_n$. When the battery is discharged to about 0.5 V, the Se 3d$_{5/2}$ peak is further shifted towards the lower binding energies and simultaneously the intensity of Mg 2p peak was increased, which indicates the formation of MgSe$_2$ and MgSe. On contrary, when the cathode was charged, the Mg 2p signals from MgSe completely vanish and Se 3p peaks shifts back to their original positions indicating that both MgSe and MgSe$_2$ transformed into metallic Se. This analysis has clearly explained the formation of polyselenides and their reversible conversion to Mg and Se. Further studies should be carried out to observe the in-situ changes and conversion reactions.

3. Recent developments in selenium-based cathodes

The exploration of many host materials for Mg$^{2+}$ ion storage have been extensively studied for high performance Mg-ion battery (MIB). These hosts include Chevrel phase compounds (Mo$_x$S$_y$, X=S, Se) [21,22], Mo$_x$Se$_y$S$_z$ (y=1, 2) [22], Cu$_x$Mo$_y$S$_z$ (x=1) [23], Mo$_x$Se$_{11}$ [24], MX$_2$ (M=Ti, Mo, W, X=S, Se) [25-28], TiS$_3$ [29], MgMSiO$_2$ (M=Fe, Mn, Co) [30-32], MgFePO$_4$F [33], and MnO$_2$ [34,35]. In most of the host cathodes, the element S and Se acted as host materials. Although the insertion of Mg ion into Mo$_x$Se$_8$ is faster than into Mo$_x$S$_8$ reflecting its high polarized anionic framework [36], but the crystal structural of host lattices was remained a challenge to explain in detail. The insertion type cathode materials for Mg-ion batteries have attracted considerable research attention due to easier the intercalation of Mg$^{2+}$. However, the strong cumblic
forces between Mg$^{2+}$ and host materials makes the Mg ion diffusion difficult into the lattices and create polarization. A rapid decline in capacity at room temperature observed is because of the failure of reversible intercalation in the lattice structure [37,38]. Therefore, a new mechanism of cathode materials was required to introduce for high performance Mg ion batteries, with high reversible reactions and without any capacity fading. As explained before the S and Se based cathode materials are conversion type electrode, where the huge structural changes and volume changes occur, which may lead to drastic fading in capacity [39]. Tashiro et al. explored a displacement type cathode material CuSe [40]. The mechanism of displacement reaction involved the insertion and extraction of Mg$^{2+}$ ions from the cathode material. In displacement type cathode materials, the transition metal ion M$^{2+}$ completely reduced to M$^{0}$ while discharging, which precipitate out as discussed in conventional conversion reaction [41-43]. The basic difference in conversion and displacement type reaction is that, in displacement type reaction, the host lattice keeps its stability before and after the reactions so there is no hikes in initial capacity and no sudden capacity fade occur as compare to conversion type cathode materials. Furthermore, the electrolytes compatibility with Mg-metal and host cathodes is very important to progress the research in Mg batteries. This review will discuss the challenges and approaches that have been employed in Mg-ion batteries keeping the Selenium metal as an interest.

Selenium metal is considered as an ideal choice to diminish the polysulfide shuttling in S-cathode. It was found that minor quantity of selenium is enough to retain the capacity retention versus Mg metal [44]. The combination of Se composite as cathode and Mg metal as an anode is considered as an ideal combination for Mg-ion storage. However the electrochemical reaction mechanism is still not defined properly [45]. Zhao-Karger et al. [20] had explained the electrochemical reactivity of Se metal with Mg anode, where they explored the Se$_n$ based cathode materials and their structural conversion during cycling. The output performance was recorded as 460 mA h g$^{-1}$ at 40 mA g$^{-1}$, with 60% capacity retention up to 10 cycles. The ex-situ Raman spectroscopic analysis was carried out to understand the structural changes of Se$_n$ to Se during electrochemical cycling. Raman spectra studies were performed on Se/CMK-3 type cathode versus Mg anode (as shown in Fig. 1(a-d)). Basically, the Se exists in different allotropes, but most stable allotrope of selenium is trigonal Se with a lattice of helical bonding in a hexagonal arrangement.
Pure crystalline form of Se exhibited Raman shift at 233 cm\(^{-1}\) reflecting trigonal bond with stretching modes of Se–Se [48,49]. Due to melt diffusion of Se chains like structures in porous CMK-3 brought Se\(_8\) molecular structures reflecting a blue shift in Raman spectra 1 at 257 cm\(^{-1}\) [50]. The conversion of Se to MgSe upon first discharge up to 0.5 V was identified by referring the MgSe compound Spectra with Raman spectra 3. During charging process, Se\(_n\) chains were formed instead of Se\(_8\), which is opposite from the peak at 233 cm\(^{-1}\), the broad peak of spectra 4 reflected the restricted accumulation of Se\(_n\) chains in narrow region of mesoporous of CMK-3. Fig. 1(d) represented the structural depiction of Se\(_8\) (ring structure) to Se\(_n\) (chain structure) during first discharge, and their subsequent conversion persist to Se\(_8\) for further charge/discharge. The Se\(_n\) (chain structure) is thermodynamically stable, and having good conductivity as compare to Se\(_8\), [51] rather S is stable in its ring from Se. Chain like structure of Se is more feasible for electrochemical oxidation of MgSe.

Furthermore, Zhao karger et al. investigated the Se–S composite based cathode i.e. SeS\(_2\)–CMK-3, with Mg anode in Mg-HMDS electrolyte. The charge–discharge potential window was set as 0.5–2.5 V at 40 mA h g\(^{-1}\), and the first discharge capacity was recorded as 600 mA h g\(^{-1}\), which was higher than discharge capacity of SeCMK-3 cathode [20]. The higher cost and scarcity problem of Se could be solved by Se\(_8\), based composite materials having good electrochemical performances. These SeSn-based cathode materials may act as a new class of materials for rechargeable Mg ion batteries.

Selenium confined in carbonaceous materials like mesoporous carbons or Se/C nanocomposites were also employed as cathode materials in non-nucleophilic electrolytes such as Mg-HMDS and BCM, which resulted in good specific capacity and rate capability [53–55]. Unfortunately, the Se-based cathode materials also have capacity fading issue due to dissolution of magnesium polyselenide (MgSe\(_n\), \(n > 2\)) in electrolytes. Yuan et al. [52] reported the novel Se/PAN based cathode material to inhibit the polyselenides dissolution in electrolytes (Fig. 1(e–i)). The unwanted intercalation of Mg were avoided and replaced with Li or Li–Mg co-intercalation by using hybrid ion electrolytes i.e. (PhMgCl)\(_2\)·AlCl\(_3\)/THF/LiCl [52]. Li addition in Mg electrolytes helped in activation of Mg battery system, as confirmed by previously studied Li–Mg hybrid battery systems [56,57]. Furthermore, the effect of synthesis temperatures on electrochemical performance of Se/PAN composites was investigated in hybrid ion electrolytes. It was noticed that lower carbonization temperature (i.e. 400 °C) may result in selenium deposition on the external surface of PAN, thus sharp decay in capacity was observed during the redox process. On the other hand, higher carbonization temperature (i.e. 450 °C) with 8:1, Se: PAN ratio and 0.4 M L\(^{-1}\) electrolyte exhibited good discharge capacity of 363 mA h g\(^{-1}\) during the first discharge. The capacity was maintained at about 216 mA h g\(^{-1}\) for 50 cycles, having capacity retention of 85% with respect to the second cycle. In addition, the rate performance was also analysed at 100, 200, 400 and 500 mA g\(^{-1}\) current densities using PAN/Se–450°C carbonized sample. In conclusion, we found that the carbonization temperature was important to synthesise a compatible PAN/Se composite cathode, which may induce good capacity and cycle performance.

The shuttled Li-ions have more tendencies to react with highly mobile cations, to keep up the capacity retention [58]. To support this claim, the reversible displacement reaction type cathode materials have been introduced such as \(\beta\)-Cu\(_2\)Se, [59] because the \(\beta\)-Cu\(_2\)Se form is a high temperature phase and good ionic conductor due to fast moving Cu\(^+\) along with a larger diffusion coefficient, as compare to low temperature \(\alpha\)-phase Cu\(_2\)Se [60–62]. The crystallography of \(\beta\)-Cu\(_2\)Se phase is presented in Fig. 2(a), where Cu ions are distributed in two interstitial sites, tetragonal (8c) and trigonal (32f) [59]. Tashiro et al. [59] synthesized \(\beta\)-Cu\(_2\)Se by two different methods i.e. solvothermal method (product was in micrometre sized) and liquid state reaction (product was in 100 nm). The capacity was increased by downsizing the method to 88% (230 mA h g\(^{-1}\)), according to theoretical capacity 260 mA h g\(^{-1}\), from 1st to 4th cycle at current density of 5 mA g\(^{-1}\) (shown in Fig. 2(c)). Ex-situ XRD analysis revealed the reversibility of displacement reaction in \(\beta\)-Cu\(_2\)Se with Mg along with 3d-crystal modelling as depicted in Fig. 2(b, d) [59]. The XRD peaks of pristine micrometre sized \(\beta\)-Cu\(_2\)Se showed in Fig. 2(d) was suppressed during discharge process, which were re-gain after charging, reflecting the reversibility of a reaction mechanism. Additionally, there are some other phases appeared after charging i.e. \(\alpha\)-Cu\(_2\)Se, CuSe\(_2\), which are low temperature phases of CuSe crystalline system. Cu ion is occupied at tetrahedral position of face centred sublattice of Se in \(\alpha\)-Cu\(_2\)Se phase, [63] though in \(\beta\)-Cu\(_2\)Se the Cu ion distributed randomly. Fig. 2(b) explains the displacement type reaction by crystal structural modelling during charging and discharging of \(\beta\)-Cu\(_2\)Se. In the discharge process, Mg ion diffused in \(\beta\)-Cu\(_2\)Se lattice to produce MgSe on same sites of FC-sublattice of Se. On the other hand, Cu ions are extruded from Se sublattice and reduced to Cu-metal. During charging, the reverse reaction of Mg and Cu ions occurred with oxidation reaction. For displacement reaction type cathode materials, the \(\beta\)-Cu\(_2\)Se with small size reflected better reversible reaction during consecutive charge/discharge cycles.

In order to sustain the cycle life with enhanced capacity, Yuan et al. [64] prepared a hybrid electrolyte based Mg battery containing non-insertion based cathode. Two different methods for Cu\(_2\)Se based material preparation were followed, such as solvothermal method for synthesis of big size particles and hydrothermal method for small sized particles. rGO was also used to verify the performance of both H–Cu\(_2\)Se (hydrothermal) and S–Cu\(_2\)Se (solvothermal) materials [64]. The small size particles synthesized by hydrothermal method (H–Cu\(_2\)Se) delivered good capacity but worse cycle performance. The Li-salt insertion into Mg-electrolyte improved the performance of battery. Furthermore, the addition of rGO nanosheets provided the conductive platform for ion transportation and enhanced the overall performance [64]. H–Cu\(_2\)Se–rGO–Mg battery produced the high capacity and better cycle performance, i.e. 243 mA h g\(^{-1}\) at 26 mA g\(^{-1}\).
with a capacity retention of 64% prolong to 20 cycles and the over potential was lower as 0.5 V. Conclusively, this study reveals the characteristic of reduced graphene oxide to improve the performance of Mg battery with hybrid electrolytes of Mg and Li.

Although for practical or commercial scale applications, the micro sized cathode materials are considerably more favourable to get higher volumetric energy density due to their higher tap density [65,66]. Zhang et al. [67] presented the novel work to evaluate the performance of micro sized particle based Se-cathode, which exhibited the high reversible magnesiation/de-magnesiation with stable cycle performance [67]. The crude copper powder was employed with Se–C based materials to compare the performance with different electrolytes, i.e. HMDS and BCM. It was realized that boron centred anion based BCM electrolyte were giving better cycle performance in Se–Cu electrode with increased capacity as compare to pristine Se powder based electrode as shown in Fig. 3(a, b). The pristine Se based cathode materials showed much bigger over potential as compare to Cu–Se based cathode materials [67]. The battery performance was recorded as 365 mA h g⁻¹ at 10 mA g⁻¹ with retention of 71% for 100 cycles. The working mechanism is presented in Fig. 3(c). The binary mixture of Cu–Se formed in-situ conversion of Cu₂Se₂ intermediates during the reduction of metallic Cu to Cu(I) and Cu(II). The discharge product including MgSe and MgCu₃Se₂ intermediates are the products of combine intercalation and displacement type reaction with Cu₃Se₂. The reversible extraction and insertion of Cu during the oxidation and reduction reaction of Cu₃Se₂ with Mg, resemble to Li-ion battery [68].

Insertion type cathode materials have been developed with very few suggestive materials for Mg ion batteries, such as MoS₂, [21,22,27] CuₓMo₆Sₓ, [69] Mg₁.0₃Mn₀.97SiO₄ [70] and TiS₂ [26]. Tungsten diselenide WSe₂ based electrode materials have been known due to its high thermal conductivity, [71] high surface energy, [72] effective p-type field effect qualities, [73] and having a layer structure metal chalcogenide. Zhao et al. proposed nanostructured WSe₂ for magnesium ion batteries. During their work, nanowires of WSe₂ were assembled over W-sheet, which acted as an efficient cathode material for intercalation/insertion of Mg batteries [74]. Chemical vapour deposition technique was employed to synthesize the in-situ growth of WSe₂ nanowire on W-foil. The battery fabrication design and working demonstration of WSe₂ nanowire based cathode film is presented in Fig. 4(a). The reversible capacity with respect to cycle numbers was examined and compared with bulk WSe powder-based cathodes. It was found that the reversible capacity and cycle life performance were much improved by nanowire based cathode material for Mg-batteries (Shown in Fig. 4(b, c)). The reversible capacity was initially obtained as 220 mA h g⁻¹ at 50 mA g⁻¹, keeping up the capacity retention up to 80% for 160 cycles, and with very low overpotential values (0.5 V). This new insertion type cathode materials comprising WSe₂ nanowire was employed to open a new direction for Mg ion batteries cathode materials.

In the beginning, Chevrel phases (CPs) were understood to be the best materials for Mg ion diffusion due to their catalytic activity [77]. CPs consists of MₓMo₆T₈ (M= metal, T=S,Se) and these host materials possessed fast cation transport mechanism, which is very unique in cathodes for Mg batteries [78-80]. The diffusion of Mg ion is affected by varia-
Fig. 3. Charge/discharge profile with BCM electrolyte (a) Se–Cu electrode (b) pristine Se electrode, (c) working principle mechanism of Se and Se–Cu electrode (Reproduced with permission [67] Copyright Wiley (2017)).

Fig. 4. (a) 3-D morphological presentation of WSe$_2$ nanowire growth on W-foil by CVD technique, (b) voltage profile of WSe$_2$ based Mg battery at 50mA g$^{-1}$, (c) cycle performance of WSe$_2$ nanowire based cathode and WSe$_2$ bulk powder based cathode at 50mA g$^{-1}$ current density (Reproduced with permission [74] Copyright ACS (2013)); (d) CV curve at scan rate of 10μm s$^{-1}$ of three electrodes synthesized by new method, (e) cycle performance of three new synthesized electrodes at 25°C at C/8 rate (Reproduced with permission [75] Copyright Wiley (2007)); (f) voltage profile Se/C cathode in BCM electrolyte at 1st, 2nd, 5th, and 10th cycles, (g) shows discharge capacities at rate performance of 0.05, 0.1, 0.25, 0.5, and 1 A g$^{-1}$, (h) cycle performance prolong to 200 cycles of Se/C cathode Vs. Mg anode at 0.66 mA g$^{-1}$ current density (Reproduced with permission [76] Copyright Wiley (2017)).
tion in temperature and composition of CPs. Selenide showed complete intercalation of Mg ion with 0 to 2 ion per unit formula without any trapping, [81] as compared to Sulfides. This trapping encounter in sulfides based CPs is mainly because of the exceptional ring arrangement of cation closely located at minimal potential energy [82,83]. When selenide is added into another structure, the distortion in selenide alters the geometry of cations, which diminish the ring arrangements and alternatively trapping of Mg-ion in the cathode. Thus, a small amount of Se is enough to boost the movements of Mg\(^{2+}\) cation in CPs. Solid solution of S and Se are also very important to discuss in CPs family of compounds, to improve the performance of Mg-ion batteries. The reduced particle size is one of the major factors to facilitate the insertion of ion in side the host materials, reflecting small diffusion lengths. Taking into account of such properties, Aurbach et al. [75] reported one new synthesis method for Mo\(_{5}S_{8}\)Se\(_{y}\) based CPs with a reduced size probably in nanometre at low synthesis temperature as compare to conventional methods, to increase the rate capability without ion trapping effect [75]. The old CPs based on sulfide Mo\(_{5}T\_8\) were made at 1200°C temperature in evacuated quartz tube. The proposed new technique was able to get pure and small crystalline based forms on Mo\(_{5}T\_8\) followed by leaching of M. Cu powder was used as M in new proposed method. The stainless steel reactor was used for single step synthesis and product was free of impurities.

Cyclic voltammetry curves from Fig. 4(d), presented the oxidation and reduction peaks of newly synthesized Mo\(_{5}S_{8}\)Se\(_{y}\) based materials (where \(y=0, 1, 2\)). The improvements in electrochemical reaction in the CPs were observed by replacing small parts of S with Se and by reducing the size of particles to nanometre. The insertion of Mg was occurred in two major steps reflecting two-phase transition in CV curve. The first peak of CV curve in all samples were broad representing the sluggish movement of Mg ion in the system, whereas the second peak was resemble to Li insertion into the same system. The replacement of Se with one or two sulfur atoms ensured the good reversibility of Mg insertion with an order of M\(_{5}0.2\)Mo\(_{5}S_{8}\)Se\(_{2}\) > M\(_{5}0.2\)Mo\(_{5}S_{8}\)Se > M\(_{5}0.2\)Mo\(_{5}S_{6}\). Cycle performance with respect to C/8 rate is shown in Fig. 4(e). The Mo\(_{5}S_{6}\)Se\(_{2}\) based cathode was utilized to maintained reversible capacity as high as 110 mA h g\(^{-1}\) at 0.12 C with capacity retention of 90%. The capacity retention was only reduced to 10% after 100 cycles as compare to lower Se concentrated samples.

Electrolytes compatibility with Mg metal is also very important to investigate with Se based cathode to increase the electrochemical performance. Anions containing high valence centre elements such as Cl, S, P, Al, As and B form well known anions, whether as Cl, F, and As form ClO\(_{4}\)\(^{-}\), PF\(_{6}\)\(^{-}\), and AsF\(_{6}\)\(^{-}\), which react with Mg metal to crudely the surface and cannot be used with Mg metal [84,85]. There are two categories of electrolytes based on anion central elements, which are compatible with Mg metal. Firstly, the Al-anions based electrolytes (also known as magnesium organohalonolaminates electrolytes), were fundamentally became the part of Mg-ion batteries research field [85,86]. The inorganic based Mg electrolytes made from the reaction of MgCl\(_{2}\) and AlCl\(_{3}\) are also included in this category [87,88]. Another category includes the Boron as a central anion element comprising anions of BH\(_{4}\)\(^{-}\), [BB\(_{4}\)\(^{-}\)]\(^{-}\), and [CB\(_{11}\)H\(_{12}\)\(^{-}\)]\(^{-}\) are employed in Mg ion batteries [84,89,90].

Zhang et al. [76] produced Se/C based composite by melt diffusion method with 50% Se loading in carbon material. The BCM electrolyte was synthesized by one step mixing of THFPB and MgF\(_{2}\) in DME solvent, to employ in a coin cell [76]. The voltage profiles of 1st, 2nd, 5th, and 10th cycles of charge/discharge of Se/C based cathode vs. Mg metal with BCM electrolyte is shown in Fig. 4(f). The initial capacity was lower but increase in consecutive cycles, the slow penetration of electrolyte in carbon spheres, and gradual involvement of Se brought high columbic efficiency reaching a high capacity of 615 Ma h g\(^{-1}\) from 7th cycle (shown in Fig. 4(g–h)). Furthermore, the over-potential was also reduced to 0.33 V. The rate performance was analysed for Se/C based cathode at 0.1, 0.2, 0.5, and 1 A g\(^{-1}\) current densities, providing capacities as 512, 477, 432, 405 mA h g\(^{-1}\), respectively (Fig. 4(g)). The rate performance and cycle performance of Se/C based cathode material with BCM electrolyte can be considered the best performance as compare to previously reported Mg-ion batteries [20,85,91,92]. The details of cathode materials, electrolytes, selenium loading and final electrochemical performance is summarized in Table 1.

### Table 1

Summary of magnesium–selenium batteries in terms of cathodes, selenium loading, electrolytes, maximum specific capacities, capacity retentions, and over potentials.

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>Cathodes</th>
<th>Se loading (%)</th>
<th>Initial Capacity (mA h g(^{-1})) Current Density [mA g(^{-1})]</th>
<th>Capacity Retentions (%) [Cycles]</th>
<th>Over potential</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-HMDS(hexamethyldisilazide)</td>
<td>Se-CM-3</td>
<td>70.5</td>
<td>460 [40]</td>
<td>60 [10]</td>
<td>0.9</td>
<td>[20]</td>
</tr>
<tr>
<td>Mg-HMDS(hexamethyldisilazide)</td>
<td>SeS(_{2})-CMK-3</td>
<td>70.5</td>
<td>600 [40]</td>
<td>60 [2]</td>
<td>1.3</td>
<td>[20]</td>
</tr>
<tr>
<td>(PMgCl(<em>{2}))–AlCl(</em>{3})–LiCl/THF</td>
<td>Se-PAN</td>
<td>45.4</td>
<td>368 [50]</td>
<td>85 [50]</td>
<td>0.2</td>
<td>[52]</td>
</tr>
<tr>
<td>Mg(AlCl(<em>{3}))Et(</em>{3})/THF</td>
<td>β–Cu(_{2})Se(100 nm)</td>
<td>81</td>
<td>230 [5]</td>
<td>88 [4]</td>
<td>0.4</td>
<td>[59]</td>
</tr>
<tr>
<td>(PMgCl(<em>{2})) AlCl(</em>{3})–LiCl/THF</td>
<td>H–Cu(_{2})Se/th GO</td>
<td>80</td>
<td>243 [26]</td>
<td>64.2 [20]</td>
<td>0.5</td>
<td>[64]</td>
</tr>
<tr>
<td>BCM electrolytes</td>
<td>Binary Se–Cu</td>
<td>40</td>
<td>365 [10]</td>
<td>71.7 [100]</td>
<td>0.5</td>
<td>[67]</td>
</tr>
<tr>
<td>Mg(AlCl(<em>{3}))Et(</em>{3})/THF</td>
<td>WSe(_{2}) nanowire</td>
<td>40</td>
<td>210 [50]</td>
<td>80 [160]</td>
<td>0.5</td>
<td>[74]</td>
</tr>
<tr>
<td>Mg(AlCl(<em>{3}))Et(</em>{3})/THF</td>
<td>Mo(<em>{5})Se(</em>{2})</td>
<td>80</td>
<td>110 [0.12C]</td>
<td>90 [100]</td>
<td>–</td>
<td>[75]</td>
</tr>
<tr>
<td>BCM electrolyte</td>
<td>Se/C</td>
<td>50</td>
<td>422 [66]</td>
<td>75 [100]</td>
<td>0.4</td>
<td>[76]</td>
</tr>
</tbody>
</table>

As discussed above Yuan et al. [52] and his co-workers made successful attempt to synthesize selenized polyacrylonitrile (Se/PAN) composite cathodes for magnesium–selenium batteries. Unlike previous reports, they used two different types of nucleophilic electrolytes with lithium salts (as additives). All-phenyl-complex electrolyte contains (PhMgCl)$_2$, AlCl$_3$, and LiCl dissolved in THF solvent (called an APC-based electrolyte), whereas the borohydride-based electrolyte contains Mg(BH$_4$)$_2$ and LiBH$_4$ dissolved in TG solvents. The electrochemical performance of different Se/PAN composite cathodes revealed different specific capacities based on Se-PAN ratio, carbonization temperatures, and carbonization times. Experimental results revealed that composite cathode synthesized at 450°C exhibited the highest values of specific capacity (225 mA h g$^{-1}$ at 100 mA g$^{-1}$ current density) with voltage platforms at about 0.9 and 1.25 V, when using APC-based electrolytes. On the other hand, synthesis time and Se-PAN ratios did not affected the capacities to large extents. It means that carbonization temperature is very crucial to obtain the optimum capacity during redox reactions. On contrary, the borohydride-based electrolyte revealed the maximum specific capacity of 190 mA h g$^{-1}$ at 100 mA g$^{-1}$ current density, which is slightly lower compared with APC-based electrolytes. The careful observation of cycle life revealed the significant capacity retentions, which confirmed the absence of side reaction owing to addition of lithium salts. Furthermore, the previous studies on magnesium-lithium hybrid ion batteries also revealed the absence of side reactions during the charging and discharging processes [10,15].

4. Future research directions

After reviewing the major progress in the development of electrolytes and electrode materials for magnesium–selenium batteries, we may reach to following opinions as future recommendations.

1. Unlike magnesium ion, magnesium–lithium hybrid ion or magnesium–sulfur batteries, magnesium–selenium batteries are less explored. The main reason could be unviability of selenium-based cathodes that are compatible with magnesium electrolytes. Thus, material scientists should focus on the synthesis of new selenium-based cathodes including selenium-carbon composites, metal-selenides, and MOF-Se composites. Efforts should be made to find suitable materials having strong physio-chemical bonding between nanoselenium and host matrix.

2. Besides selenium cathodes, the preparation of compatible electrolyte solutions is very important to develop the magnesium–selenium batteries. Both organic and inorganic magnesium salts and their solvents with high solubility/conductivity should be investigated thoroughly to minimize the magnesium–selenium polyselenide shuttle effect. Chemical researchers should put focus on optimization of electrochemistries of magnesium–selenium batteries with improved working voltages to get their practical realizations.

3. Furthermore, attempts should be made to develop the alternative strategies to confine the selenium during redox reactions. These strategies could be usage of graphene or carbon nanotubes coatings on selenium cathodes.

4. Development of vanadium-doped metal selenides should be carried out to synthesize a selenium cathode that can exhibit high working voltage and resist against polyselenides dissolutions into an electrolyte.

5. The investigation on the working mechanism of magnesium–selenium battery is still at the initial stage, thus further research is compulsory to fully understand the nature of reactions and conversion rates.

5. Conclusions

In conclusion, various types of selenium based cathode materials are critically reviewed as magnesium–selenium batteries. These selenium cathodes include different metal selenides, and selenium–carbon composites. Furthermore, this review focused on exploration of different types of electrolytes including hybrid electrolytes to get stable and high specific capacity with minimized shuttle effects. It was found that BCM electrolytes have been observed as best electrolytes for Se/C based cathode materials. It was also noticed that the selenium insertion could overcome the polysulfide formation with sulfur, which can overcome the capacity fading. Compared with sulfur electrodes, the small loading of selenium is more effective to achieve high electrochemical performances. We hope this review article will uncover the new research directions for researchers working on magnesium ion technology in the near future.

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References
