Abstract: Rechargeable magnesium (Mg)-based energy storage has attracted extensive attention in electrochemical storage systems with high theoretical energy densities. The Mg metal is earth-abundant and dendrite-free for the anode. However, there is a strong Coulombic interaction between Mg$^{2+}$ and host materials that often inhibits solid-state diffusion, resulting in a large polarization and poor electrochemical performances. Herein, we develop a Mg–Li hybrid battery using a Mg-metal anode, an FeSe$_2$ powder with uniform size and a morphology utilizing a simple solution-phase method as the counter electrode and all-phenyl-complex/tetrahydrofuran (APC)/LiCl dual-ion electrolyte. In the Li$^{+}$-containing electrolyte, at a current density of 15 mA g$^{-1}$, the Mg–Li hybrid battery (MLIB) delivered a satisfying initial discharge capacity of 525 mAh g$^{-1}$. Moreover, the capacity was absent in the FeSe$_2$|APC|Mg cell. The working mechanism proposed is the “Li$^{+}$-only intercalation” at the FeSe$_2$ and the “Mg$^{2+}$ dissolved or deposited” at the Mg foil in the FeSe$_2$|Mg$^{2+}$/Li$^{+}$|Mg cell. Furthermore, ex situ XRD was used to investigate the structural evolution in different charging and discharging states.

Keywords: Mg–Li hybrid batteries; magnesium batteries; FeSe$_2$; metal anode

1. Introduction

The application of magnesium (Mg)-based energy storage technologies in high energy density electrochemical storage systems has attracted increasing attention. The reason why magnesium-based batteries has attracted extensive attention, recently—especially in Mg-metal anode (“negative”) batteries—is that Mg is cheap, readily available and has a reasonable reduction potential (−2.4 V vs. SHE) and large specific volumetric capacity of 3833 mAh cm$^{-3}$ (a two-electron transfer process) [1–3]. Additionally, most importantly, rapid deposition and/or exfoliation of Mg is possible in compatible electrolytes without forming dendritic structures [2,4]. However, there is an obstacle to the application of Mg-based energy storage due to its bivalent cation, namely, a strong Coulombic interaction between Mg$^{2+}$ ions (which have higher charge densities than monovalent) and the host materials. This often results in slowing the solid-state diffusion—which then leads to significant polarization and poor electrochemical performance [5,6]. In order to overcome these problems, one approach is to develop better bivalent Mg-ion host cathode materials. Another is to utilize a suitable electrolyte system with Mg-metal anode.

To date, many studies have focused on the cathode materials. The representative cathode materials for rechargeable Mg batteries has been intercalation materials, including Chevrel-phase materials (Mo$_6$X$_8$; X = S, Se) [7–9], layered MX materials (where M is a metal; X = S, Se), i.e., TiS$_2$, FeS$_2$, TiSe$_2$,
WSe₂, CoSe₂) [10–14], spinel compounds (spinel λ-Mn₂O₄ and sulfur spinel compounds (Mn₂S₄, Cr₂S₄, Ti₂S₄)) [15–17], layered oxide materials (V₂O₅, α-MoO₃, TiO₂, etc.) [18–22] and polyanion materials (transition metal silicates and phosphates) [23–27]. Instead of intercalation materials, the conversion materials have also been important research objects. For example, transition metal oxides (α-MnO₂, δ-MnO₂) [28–31], chalcogenide (CuS, Cu₂−xSe) [32–35], chloride (AgCl) [36] and organic compounds (quinone-based polymers and 2,5-dimethoxy-1,4-benzoquinone (DMBQ)) [37,38]. In addition, it has been found that trace water in the electrolyte could be beneficial for interfacial ion transfer and the ionic diffusion under study. This was named as water co-intercalation materials (α-V₂O₅, δ-MnO₂) [16,30,31]. However, among these materials, only a few exhibit available performance of the Mg-ion battery (MIB). The main reason is the sluggish transportation of Mg ions in the host material.

In order to overcome the obstacle of Mg-ion sluggish solid–state diffusion, the elemental redox chemistries (Mg/O₂, Mg/S, Mg/I₂, Mg/Se) [39–45] and Mg²⁺/Li⁺ (Mg–Li) ion, Mg²⁺/Na⁺ (Mg–Na) ion, Mg²⁺/Zn²⁺ (Mg–Zn) of ion dual-salt electrolyte systems [26,46–56] has been investigated. Mg–Li hybrid batteries (MLIBs) with NaV₅O₈·1.69H₂O (NVO) nanobelts as the cathode and Mg metal as the anode exhibit a high rate capability. The reaction mechanism is the Li⁺ intercalation—along with a small amount of Mg²⁺ adsorption at the cathode during the discharging process—whereas the anode side is dominated by Mg²⁺ deposition/dissolution [53]. The sulfur compounds and oxide materials (MoS₂, TiS₂, TiO₂, etc.) have also functioned well in hybrid cells with Li⁺-containing APC electrolytes [47–49]. In this regard, the Mg–Li hybrid ion battery is an ideal choice.

During the development of cathode materials—in order to decrease anion polarizability—selenides were investigated as cathodes due to their demonstrated or projected good ionic mobility. Nickel–iron (Ni–Fe) bimetallic diselenides microflowers (Ni₉.₇₅Fe₀.₂₅Se₂, NFS) had been reported [57] as cathodes for rechargeable Mg batteries. The NFS delivered a considerable specific capacity of 190 mAh g⁻¹ at 10 mAh g⁻¹ in APC electrolyte. Hence, iron diselenide (FeSe₂) is a promising candidate material for rechargeable Mg batteries or MLIBs because of its suitable band-gap energy (Eg = 1.0 eV) and good conductivity. The Mg–Li dual salt electrolytes could be used to obtain rapid ion transport within the cathode while maintaining the utility and benefits of an Mg anode.

Herein, FeSe₂ powder with uniform size and morphology using a simple solution-phase method was fabricated according the previous report [58] and used as the cathode materials for the MLIBs. Besides the physical investigation for the FeSe₂, an electrochemical characterization is carried out for the MLIBs system. The MLIBs system had improved the performance over the rechargeable Mg batteries with the FeSe₂ cathode. MLIBs with FeSe₂ cathode demonstrating a high initial discharge specific capacity (525 mAh g⁻¹ at 15 mA g⁻¹) and relatively good rate capabilities. Moreover, no obvious capacity or voltage plateau was observed for FeSe₂ in the APC electrolyte system. In this hybrid cell system, Li⁺ intercalation occurs reversibly at the cathode material due to its superior mobility compared to divalent magnesium. Mg strips and plates first appeared at the anode as a result of a higher redox potential (~2.37 V) than Li⁺/Li⁺ (3.04 V).

2. Experimental Section

2.1. Synthesis of FeSe₂

All reagents were obtained from Sigma-Aldrich as analytical grade and ready-to-use without further refinement. In a 100-mL three-necked flask, 30 mL of oleylamine (OM) and 20 mL of 1-octadecene (ODE) were added at room temperature and heated under nitrogen at 120 °C for 30 min. Then, 2 mmol of FeCl₂·4H₂O powder was added to the solution. After stirring vigorously for 30 min, a solution of selenium powder (4 mmol) or OM (8 mL) was added to the flask and stirred for 10 min. The solution temperature rose to 150 °C and was maintained for 30 min before cooling to room temperature. After reaction, excessive ethanol was added to the solution to precipitate the FeSe₂ nanoparticles. The precipitate was washed repeatedly with hexane and ethanol, and the product was collected by
centrifugation. Then the material was obtained after drying in a vacuum oven. This was prepared according to a previous report [58].

2.2. Preparation of Electrolyte

The all-phenyl-complex/tetrahydrofuran solution (APC, 0.4 M) was prepared according to a previous report about two-step procedure in the argon-filled glove box [59]. Initially, 0.267 g of aluminum trichloride (AlCl₃, anhydrous, 99.99%) was slowly added to 3 mL of tetrahydrofuran (THF, anhydrous, ≥99.9%) with vigorous stirring to form an AlCl₃–THF solution. Then, 2 mL of phenyl magnesium chloride (2-M solution in THF) was added dropwise to the AlCl₃–THF solution. This solution was vigorously stirred for at least 24 h before being used. Due to the exothermic nature of the above prepared solutions, it is worth noting that their preparation should include cooling. The dual salt (Mg²⁺/Li⁺) electrolyte was prepared by adding an appropriate amount of LiCl (0.4 M) to the 0.4-M APC electrolyte. The mixture was stirred for at least 12 h prior to use. The electrolyte is sensitive to moisture and oxidation, so all processes should be performed in a glove box (H₂O/O₂ levels < 0.1 ppm) under argon gas protection.

2.3. Material Characterization

The crystalline structures of samples were identified by X-ray powder diffraction (XRD) using a Rigaku D/max-2500 (Cu Kα radiation, λ = 0.15405 nm, 40 kV/200 mA), within diffraction angles 2θ from 20° to 70° at step size of 0.02°. The sample microstructures were characterized using a JEOL 6701 F field-emission scanning electron microscope (FE-SEM).

2.4. Cells Assembling and Electrochemical Measurements

The slurry was comprised of FeSe₂ and super P (SP; 80 wt% and 10 wt%, respectively) with 10 wt% poly (vinyl difluoride) (PVDF) in an N-methyl-2-pyrrolidone (NMP) solution. The doctor blade was employed to coat the slurry onto copper foil (99.6%, Goodfellow). After drying at 80 °C for 12 h, it was punched into disk electrodes with a diameter of 1 cm. The active material loading was about 1 mg cm⁻². Study of the electrochemical performance of the FeSe₂ involved the use of CR2032 coin-shaped cells with the working FeSe₂ electrode, an Mg foil as the counter electrode, Whatman borosilicate glass fiber paper as the separator and 180 µL of 0.4-M APC with and without Li⁺ as the electrolyte. Cycling performances and rate capabilities were measured by an Arbin BT2000 system from 0.3 V to 1.6 V versus Mg²⁺/Mg. The current density was calculated using the mass percent of FeSe₂ nanoparticles in the electrodes. Cyclic voltammograms (CVs) were obtained using an Autolab electrochemical workstation (PG302 N) at the same potential range (0.3–1.6 V) and scan rate (0.1 mV s⁻¹, vs. Mg²⁺/Mg). All electrochemical measurements were carried out at 25 °C.

2.5. Preparation of Ex Situ XRD Samples

To prepare the Mg-containing samples, the pure FeSe₂ electrode was discharged to 0.3 V vs. Mg at a constant current of 50 mA g⁻¹ while the demagnesiated sample electrodes were charged to 1.6 V vs. Mg. In order to obtain ex situ XRD samples, all cells were disassembled in an inert atmosphere. Moreover, all electrodes were repeatedly washed with THF, then dried overnight at 25 °C to remove excess electrolyte adhering to the surface in an inert atmosphere.

3. Results and Discussion

FeSe₂ nanoparticles were synthesized under nitrogen using a simple solution-phase method based on a previous report about synthetic procedure and featured uniform sizes and morphologies [58]. The synthesis procedure of FeSe₂ is shown in Figure 1. FeCl₂·4H₂O powder and selenium dissolved in OM were sequentially added to a mixed solution of OM and ODE. During the reaction, the FeCl₂·4H₂O precursor solution gradually became reddish-yellow. After selenium injection and increasing the
temperature to 150 °C, the color of the solution gradually turned black. The reddish yellow solution was the reaction between FeCl$_2$ and OM which can lead to formation of a Fe–OM complex while the black solution was formed of putting Se–OM solution into above solution in order to the formation of FeSe$_2$.

![Figure 1. Synthetic route to FeSe$_2$.](image)

The XRD pattern of the as-prepared FeSe$_2$ is shown in Figure 2a, suggesting an orthorhombic FeSe$_2$ structure. The diffraction peaks of the obtained sample matched well with PDF#79-1892 card of FeSe$_2$ Pnnm space group with a lattice parameter $a = 4.804$ Å, $b = 5.784$ Å and $c = 3.586$ Å. The 20 value of diffraction peak was 31.10, 34.83, 36.23, 48.20, 50.89, 53.95 and 64.05°, respectively. No peaks of any other phases were observed, and the sharp peaks imply the high crystalline structure. It indicated that only high-purity FeSe$_2$ was found in the black solution. The probable reaction mechanism for the formation of FeSe$_2$ was to form a Fe–OM complex through adding the FeCl$_2$·4H$_2$O powder into the OM/ODE solution. FeSe$_2$ nuclei quickly formed upon the addition of the Se–OM solution and gradually grew over time, ultimately reaching a certain size. The sizes of FeSe$_2$ nanoparticles were well controlled due to the use of OM ligands to protect the surfaces of the material. A scanning electron microscopy (SEM) image of FeSe$_2$ powder are shown in Figure 2b. The SEM confirmed that the FeSe$_2$ had a nanosized dimension, which would be beneficial for enhancing the Mg and Li-ion insertion/extraction during the electrochemical reaction. The nanoparticle of FeSe$_2$ was about 100–300 nm. However, the SEM shows that the FeSe$_2$ nanoparticles were aggregated, and the size of the agglomerate reaches the micron level. This phenomenon had a negative impact on the Mg-ion insertion/extraction because of the serious size-dependence of magnesium storage.

![Figure 2. Characterization of FeSe$_2$ nanoparticles. (a) XRD spectrum; (b) SEM image of FeSe$_2$.](image)

Figure 3a,b shows the CV curves of the FeSe$_2$ electrodes recorded using APC electrolyte with and without LiCl, respectively. It can be observed that the curves of the first cycle was different from the subsequent cycles. For the initial Li$^+$-containing electrolyte cycle (scanned from an open circuit potential of ~1.65 V, all subsequent potentials now referring to Mg/Mg$^{2+}$), a cathodic broad peak clearly appeared at 0.58 V can be attributed to the solid electrolyte interphase (SEI) layers formation resulting from the electrochemically driven electrolyte degradation and the decomposition of FeSe$_2$ (FeSe$_2$ + 2Li$^+$ + 2e$^-$ → FeSe + Li$_2$Se, FeSe + 2Li$^+$ + 2e$^-$ → Fe + Li$_2$Se) (Figure 4a) [60,61]. Two anodic peaks appeared at approximately 1.21 and 1.56 V in the subsequent CV scans in the first cycle, respectively, which should be ascribed to the formation of the Li$_x$FeSe and FeSe (Fe + Li$_2$Se →
$\text{Li}_x\text{FeSe} + (2-x)\text{Li}^+ + (2-x)e^- \rightarrow \text{FeSe} + x\text{Li}^+ + xe^-$, respectively (Figure 4a) [60,61]. During the subsequent cycles, both peak intensity and positions changed. There were two cathodic peaks at $\approx 0.61$ and $1.06$ V, which could be corresponded to the decomposition of FeSe$_x$ and FeSe. While two anodic peaks appeared at $\approx 1.16$ and $1.48$ V, it could be ascribed to the formation of the Li$_x$FeSe and FeSe. It exhibited a relatively high symmetry with cathodic peak and anodic peak, but the current density of cathode/anode peak gradually decreased with increasing cycles. This is likely that due to the reversible phase transition induced by Li$^+$ intercalation and deintercalation in the Li$^+$-containing electrolyte. In contrast, in the APC electrolyte without addition of LiCl, cathodic and anodic peaks appeared in the first cycles. The subsequent cycles showed negligible currents, indicating that the Mg$^{2+}$ was almost irreversible for the FeSe$_x$ electrode. These peaks were corresponded to small plateaus presented in the charge–discharge curves (Figure 3c,d).

Figure 3. CV curves of (a) FeSe$_2$|Mg$^{2+}$/Li$^+$|Mg cell and (b) FeSe$_2$|Mg$^{2+}$|Mg cell; charge–discharge curves of (c) FeSe$_2$|Mg$^{2+}$/Li$^+$|Mg cell and (d) FeSe$_2$|Mg$^{2+}$|Mg cell; (e) cycling performance and Coulombic efficiency of FeSe$_2$|Mg$^{2+}$/Li$^+$|Mg cell; (f) rate capability of FeSe$_2$|Mg$^{2+}$/Li$^+$|Mg cell.
Figure 4. XRD patterns of the FeSe$_2$ electrode in (a) FeSe$_2$|Mg$^{2+}$/Li$^+$|Mg cell and (b) FeSe$_2$|Mg$^{2+}$|Mg cell at different discharging/charging states.

Figure 3c,d showed the charge–discharge curves of the FeSe$_2$ electrode cycled at constant specific current (15 mA g$^{-1}$) using APC electrolyte with and without LiCl, respectively. In the Li$^+$-containing APC electrolyte, the FeSe$_2$|Mg$^{2+}$/Li$^+$|Mg cell delivered initial specific capacities of 525 and 287 mAh g$^{-1}$ with a low Coulombic efficiency of 55%, respectively, although the capacities decreased with the increase of cycle number. This capacity value was significantly higher than the FeSe$_2$|Mg$^{2+}$|Mg cell. For the APC electrolyte without LiCl, the FeSe$_2$|Mg$^{2+}$|Mg cell delivered initial discharge and charge capacities of 42 and 11 mAh g$^{-1}$, respectively. Moreover, it delivered very little capacity during subsequent cycles. These results were consistent with the CV curves and had shown that the reaction mechanism of this material in the Mg–Li hybrid (or dual salt) cell may be attributed to lithiation/delithiation rather than magnesiation/demagnesiation.

The cycling performances and Coulombic efficiency of FeSe$_2$|Mg$^{2+}$/Li$^+$|Mg battery are illustrated in Figure 3e. As is seen from the curves, the specific capacities decreased with the increase of cycles. In addition—despite a lower Coulombic efficiency observed in the first and second cycles—the Mg–Li hybrid battery showed a highly reversible behavior during subsequent cycles. The chloride ion was the counter-ion for the lithium salt, which made up a part of APC, and LiCl was expected to be very compatible with APC. The formed APC–LiCl electrolyte was conducive to highly reversible Mg deposition and/or dissolution and afforded a high anodic stability, despite the reaction between LiCl and the complex Mg electrolyte [62]. Low initial Coulombic efficiencies at first may be due to the SEI formation. For comparison, the rate capabilities of the FeSe$_2$|Mg$^{2+}$/Li$^+$|Mg battery under various current densities are shown in Figure 3f. Raising the current density from 15 mA g$^{-1}$ to 150 mA g$^{-1}$, the capacity decreased the increase of current density. This reflected a relatively favorable capability during short cycling. The results showed that the performance of the MLIBs was superior to the traditional rechargeable Mg battery.

The electrochemical reaction mechanism of the FeSe$_2$ was further investigated by ex situ X-ray diffraction (XRD) test at different discharging/charging states in APC electrolytes with and without LiCl. The results are shown in Figure 4a,b, respectively. In the Li$^+$-containing electrolyte, the “Li$^+$-only intercalation” mechanism at the cathode was confirmed after a comparison of XRD patterns before and after discharging (Figure 4a). After discharging at first time, the Li$_2$Se, Fe and FeSe were detected, it can be attributed to the solid electrolyte interphase (SEI) layers formation resulting from the electrochemically driven electrolyte degradation and the decomposition of FeSe$_2$ (FeSe$_2$ + 2Li$^+$ + 2e$^-$ → FeSe + Li$_2$Se, FeSe + 2Li$^+$ + 2e$^-$ → Fe + Li$_2$Se) [60,61]. This confirmed that only Li$^+$ reacted with FeSe$_2$ in the mixed-ion electrolyte and was consistent with the CV and charge–discharge curves. However, after charging at first time, the FeSe was detected rather than FeSe$_2$. Which should be ascribed to the formation of the Li$_{2-x}$FeSe and FeSe (Fe + Li$_2$Se → Li$_{2-x}$FeSe + (2-x)Li$^+$ + (2-x)e$^-$, Li$_x$FeSe → FeSe + xLi$^+$ + xe$^-$), respectively [60,61]. In the plain APC electrolyte, the FeSe$_2$ structure remained unchanged during the charge–discharge process (Figure 4b).
Based on the above analyses, a proposed mechanism is shown in Figure 5. Since Li\(^+\) ions are completely supplied though the electrolyte, this hybrid battery requires high Li\(^+\) concentrations of more than 0.4-M in the electrolyte to function at high capacities.

![Figure 5. Schematic of the working mechanism of the FeSe\(_2\)/Mg\(^{2+}\)/Li\(^+\)/Mg battery.](image)

4. Conclusions

This study developed a Mg–Li hybrid battery using a Mg-metal anode, an FeSe\(_2\) powder with uniform size and morphology utilizing a simple solution-phase method as the counter electrode and an 0.4-M APC electrolyte with 0.4-M LiCl additive. FeSe\(_2\) was proved to be a promising cathode material for the Mg\(^{2+}\)/Li\(^+\) hybrid electrolyte of rechargeable Mg-anode batteries. In the Li\(^+\)-containing electrolyte, at a current density of 15 mA g\(^{-1}\), the MLIB delivered satisfying initial discharge capacity of 525 mAh g\(^{-1}\) and charge capacity of 287 mAh g\(^{-1}\), respectively. However, the capacity was absent in the FeSe\(_2\)/Mg\(^{2+}\)/Mg cell. The proposed working mechanism was the “Li\(^+\)-only intercalation” at the FeSe\(_2\) and the “Mg\(^{2+}\) dissolved or deposited” at the Mg foil in the FeSe\(_2\)/Mg\(^{2+}\)/Li\(^+\)/Mg cell. The electrolyte provided all the high concentrations of Li\(^+\) needed, in order that the Mg–Li hybrid battery can function at high capacities.

Author Contributions: C.Z., L.Z. and N.L. carried out the material laboratory work, participated in the design of the study and the manuscript structure; C.Z. collected field data and drafted the manuscript; L.Z., N.L. and X.Z. participated in data analysis and critically revised the manuscript. All authors gave final approval for publication and agree to be held accountable for the work performed therein. All authors have read and agreed to the published version of the manuscript.

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