Insights into Mg\(^{2+}\) Intercalation in a Zero-Strain Material: Thiospinel Mg\(_x\)Zr\(_2\)S\(_4\)

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§Supporting Information

ABSTRACT: The Mg battery cathode material, thiospinel Mg\(_x\)Zr\(_2\)S\(_4\) (0 ≤ x ≤ 1), exhibits negligible volume change (ca. 0.05%) during electrochemical cycling, providing valuable insight into the limiting factors in divalent cation intercalation. Rietveld refinement of XRD data for Mg\(_x\)Zr\(_2\)S\(_4\) electrodes at various states of charge, coupled with EDX analysis, demonstrates that Mg\(^{2+}\) can be inserted into Zr\(_2\)S\(_4\) at 60 °C up to x = 0.7 at a C/10 rate (up to x = 0.9 at very slow rates) and cycled with a high Coulombic efficiency of 99.75%. HAADF-STEM studies provide clear visual evidence of Mg-ion occupation in the lattice, whereas XAS studies show that Zr\(^{4+}\) was reduced upon Mg\(^{2+}\) intercalation. Operando and synchrotron XRD studies reveal the creation of two phases during the latter stages of discharge (x > 0.5) as the lattice fills and Mg\(^{2+}\) ions begin occupying tetrahedral (8a) sites in addition to octahedral (16c) interstitial sites. Compared to the isostructural Ti\(_2\)S\(_4\) thiospinel, Zr\(_2\)S\(_4\) presents a slightly larger cell volume and hence an almost ideal zero-strain lattice on Mg\(^{2+}\) insertion. Nonetheless, its 4-fold lower electronic conductivity results in a diffusion coefficient for Mg\(^{2+}\) ions (D\(_{Mg^{2+}}\) 1 × 10\(^{-10}\) to 1 × 10\(^{-9}\) cm\(^2\)/s) that is more than a factor of 10 lower than in Ti\(_2\)S\(_4\). This shows that delocalization of the electron charge carriers in the framework is a very important factor in governing multivalent ion diffusivity in the thiospinel framework and, by extension, in other materials.

INTRODUCTION

To utilize renewable resources and reduce fossil fuel consumption, energy storage technology is needed that surpasses the Li-ion batteries that currently dominate the global market. Magnesium batteries are a promising alternative because of the abundance, inherent safety, relatively low reduction potential (−2.37 vs SHE), and exceptionally high volumetric capacity (3,832 mAh/cm\(^3\)) of the Mg metal negative electrode. \(^{1,5,6}\) Despite these benefits, magnesium battery technology is plagued by the lack of suitable intercalation electrode materials and electrolytes that are stable at high potentials. Because of its divalent charge, Mg\(^{2+}\) experiences much stronger interactions with its host lattice in comparison to monovalent cations. These interactions often cause electrode materials to exhibit poor Mg\(^{2+}\) solid state diffusion,\(^{7,8}\) and promote a tendency to convert upon insertion\(^{9,10}\) that results in the formation of impenetrable layers on the surface of the electrode material. As a divalent cation, Mg\(^{2+}\) also experiences strong ion pairing and solvent interactions in solution that can lead to a large desolvation penalty at the electrode—electrolyte interface, which serves as an additional barrier to intercalation.\(^{11,12}\)

To compete with Li-ion cells, the Coulombic efficiency of both positive and negative electrodes in Mg\(^{2+}\) battery systems must also be improved to attain cycle life closer to typical Li-ion technology (i.e., > 500 cycles). As an example, thiospinel Mg\(_2\)Ti\(_2\)O\(_4\) delivers a reversible energy density of 230 Wh/kg, but with a Coulombic efficiency of only 99%.\(^{13}\) In a cell without excess Mg, such a Coulombic efficiency would limit the cell to about 70 cycles before it could only deliver 50% of its initial capacity. Low Coulombic efficiencies can be caused by a range of possibilities,\(^{14}\) but one common source is the expansion, shrinkage, and consequent cracking of the active material during cycling. \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) has found commercial success as a Li-ion battery negative electrode due to its lack of volume change during cycling, yielding an impressive cycle life (>5,000 cycles).\(^{15}\) By minimizing structural changes upon (de)intercalation, such “zero-strain” materials exhibit enhanced stability and electrochemical performance.

Highly reversible Mg\(^{2+}\) positive electrode (cathode) intercalation materials that have been reported (the metallic
Chevrel phase Mo$_2$S$_x$ and electronically conductive layered-TiS$_4$/spinel-Ti$_2$S$_3$ are able to reversibly cycle Mg$^{2+}$ by utilizing a soft, polarizable anion-sulfide lattice that exhibits relatively weak interactions with the mobile ions. Density functional theory demonstrates that the metallic nature of the Mo$_2$S$_x$ host provides fast, responsive electronic screening that shields the charge of Mg$^{2+}$, promoting its good mobility in this structure. The performance of some of the sulfide materials was further improved by operating cells at elevated temperatures to better overcome energetic barriers for insertion into, and diffusion through, the host. Despite these kinetic advantages, sulfides present high mass and low operating voltages, which leads to poor energy densities. It is theoretically possible to increase the operating voltage by using transition metals with high theoretical redox potentials such as Cr$_2$S$_4$; however, attempts to do so have failed to produce notable electrochemical reversibility.

This is thought to be due to significant overlap between the sulfur 3p and transition metal 3d orbitals in these compounds, which effectively means that anion redox (S$^{2−}$/S$^{-}$) would govern the electrochemistry. The formation of electron holes in the sulfur 3p states is not favorable, rendering these materials electrochemically inactive.

Cathode materials for magnesium intercalation with high energy densities can theoretically be obtained by using a lightweight and high-voltage oxide lattice. However, these compounds often favor conversion (to form MgO and stable transition metal oxides) over the intercalation of Mg$^{2+}$ due to the highly polarizing nature of the O$^{2−}$ anion. After years of research efforts, corrosion-free electrolytes now exist that can resist oxidation up to 3.2 V (vs Mg), which is sufficient for an intercalation cathode with an average discharge potential of about 2.5 V. It would be advantageous to use oxides to obtain high voltage cathode materials so that Mg batteries could compete with the energy density of Li-ion batteries; however, Mg$^{2+}$ solid state diffusion must be improved before oxides can reversibly cycle this divalent ion. By studying systems that are capable of reversible Mg$^{2+}$ intercalation, it is possible to isolate the key factors that affect Mg$^{2+}$ diffusivity in solid lattices. These aspects can then be optimized to design electrode materials.

Potential factors that limit diffusion rates include (1) restricted physical pathways for ion migration that lead to high activation energy barriers; (2) interactions of the divalent cation with either the anions and/or existing intercalated cations within the lattice; and (3) a lack of screening of the high positive cation charge by itinerant electrons in the host cations within the lattice; and (3) a lack of screening of the restricted physical pathways for ion migration that lead to high activation energy barriers.

In the positive electrode assuming a maximum of 1 Mg$^{2+}$ can intercalate per Zr$_2$S$_4$ unit. This capacity was used for determining the theoretical capacity was determined by the amount of active material and then dried at elevated temperature to remove NMP. The lattice was lithiated by stirring CuZr$_2$S$_4$ powder in excess $n$-butyllithium for 7 days at room temperature inside an Ar-filled glovebox because of the highly flammable nature of the reagent used. The product was chemically oxidized with excess I$_2$ to clean Cu from the surface and remove lithium from the lattice. The final product, cubic Zr$_2$S$_4$, was collected.

A Zeiss field emission scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDX) detector was used to examine material morphologies and elemental compositions. Samples were transferred to the instrument with minimal exposure to air, and scans were collected at an accelerating voltage of either 15 or 20 keV.

Zr$_2$S$_4$ electrodes were prepared in an Ar-filled glovebox by mixing the oxidized material with Super P and polyvinylidene fluoride (PVDF, average Mn$_{P}$ ~ 534 000) in an 8:1:1 weight ratio in N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich 99.5%). This mixture was ground for several minutes before the slurry was cast onto Mo foil and then dried at elevated temperature to remove NMP. The theoretical capacity was determined by the amount of active material in the positive electrode assuming a maximum of 1 Mg$^{2+}$ can intercalate per Zr$_2$S$_4$ unit. This capacity was used for determining the C-rate and x values in Mg$_x$Zr$_2$S$_4$.

The All-Phenyl Complex (APC) electrolyte was synthesized following a slightly modified literature procedure, with tetrahydrofuran (THF) or tetraglyme (G4) as the solvent. Prior to the preparation of APC in G4, excess solvent was removed from the phenylmagnesium chloride precursor through evaporation under vacuum at room temperature for 12 h in order to crystallize C$_6$H$_4$MgCl·6THF. The synthesis of magnesium monocarborane (MMC) in tetraglyme (G4) electrolyte has been described previously. These electrolytes were prepared without exposure to air or water to ensure safe handling of the required reagents.

All electrochemical characterization was performed on cells assembled/materials stored in an Ar-filled glovebox. Cycling studies were performed by assembling coin cells (2325) using polished Mg as the counter electrode and a glass fiber separator. Galvanic Interruption Titration Technique (GITT) experiments were carried out using ConFlat cells with three layers (of dry) glass fiber filter paper as separators and Mg foil as the reference and counter electrodes. All electrochemistry was measured with a Biologic VMP3 potentiostat while cells were held at 60 °C in a thermostated oven. Electrical conductivity was measured using a standard DC four-point probe method.

Scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) characterization studies were carried out on a FEI Titan cubed 80–300 STEM operated at 200 kV.
Figure 1. XRD Rietveld refinement of (a) CuZr₂S₄ (blue asterisks mark the reflections that disappear upon removal of Cu) and (b) Zr₂S₄ that shows experimental data (black crosses), fitted profile (red line), difference map between observed and calculated data (blue line), and Bragg positions of the Fd₃m spinel phase (green ticks). The insets show the crystal structure of the Fd₃m spinel phase comprised of ZrS₄ (green octahedra); in CuZr₂S₄ the Cu ions are shown as blue circles. Experimental atomic resolution (c) HAADF-STEM and (d) ABF-STEM images of the oxidized Zr₂S₄ along the [011] zone axis. Corresponding multislice simulated images are delineated by white and black boxes in the top left corner of each figure, and the projected atomic structures shown in the bottom right corner mark Zr atomic sites with higher and lower number of Zr atoms within the atomic column (dark and light green circles, respectively). S atomic sites (yellow circles) are superimposed onto the experimental images.

Table 1. Mg²⁺ and Cu²⁺ Occupancies in MgₓCuₓZr₂S₄ as Determined by Rietveld Refinement of XRD, and Electrochemistry, with EDX for Comparison

<table>
<thead>
<tr>
<th>Cuₓ (top) and Mgₓ (bottom) content in MgₓCuₓZr₂S₄</th>
<th>lattice parameter, a (Å)</th>
<th>XRD Rietveld Refinement</th>
<th>electrochemical</th>
<th>EDX</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine, CuZr₂S₄</td>
<td>10.3968(1)</td>
<td>0.950(6)</td>
<td>0.93(12)</td>
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<tr>
<td>oxidized, Zr₂S₄</td>
<td>10.3561(2)</td>
<td>0.063(6)</td>
<td>0.08(1)</td>
<td></td>
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<tr>
<td>partially discharged, Mg₀.₆Zr₂S₄</td>
<td>10.3540(5)</td>
<td>0.31(5)</td>
<td>0.39</td>
<td>0.32(5)</td>
</tr>
<tr>
<td>fully discharged, Mg₀.₇Zr₂S₄</td>
<td>10.3607(4)</td>
<td>0.54(5)</td>
<td>0.77</td>
<td>0.76(2)</td>
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<tr>
<td>phase 1: 43(2)%</td>
<td></td>
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<tr>
<td>phase 2: 57(2)%</td>
<td></td>
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<td></td>
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<tr>
<td>total 0.74(4)</td>
<td></td>
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<tr>
<td>recharged, Mg₀.₅Zr₂S₄</td>
<td>10.3597(5)</td>
<td>0.08(6)</td>
<td>0.16</td>
<td>0.11(4)</td>
</tr>
</tbody>
</table>

“The lattice parameters for the cubic Fd₃m phases are also included, which emphasize the formation of a larger cell volume phase only in the latter half of discharge. Mg²⁺ insertion and removal was carried out at a C/20 rate.

and equipped with a high-brightness field-emission gun (X-FEG), aberration correctors on probe- and image-forming lens systems, a monochromator and a Gatan image filter Quantum-965 spectrometer. Atomic-number sensitive (Z-contrast) high-angle annular dark-field (HAADF) images and annular bright-field (ABF) images were obtained at the beam convergence semiangle of 19.1 mrad using a detector angular range of 79.5−200 mrad and 10−20 mrad, respectively. Multislice HAADF-STEM image simulations were performed using Dr. Probe software with the same microscope parameters as the experimental imaging condition. In order to take the effect of a probe spread function into account, all of the simulated images were convolved by a Gaussian with the full-width at half-maximum of 0.04 nm. The EELS images were recorded with 1 eV dispersion of the spectrometer to include Mg K-edge and Zr L₂,₃ and S k-edges in a single spectral image. EELS data were acquired with a beam current of 400−500 pA and a pixel dwell time of 20 ms to maximize the signal-to-noise ratio while minimizing the beam damage artifacts.

X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data were collected in transmission mode at the 20-BM beamline of Argonne’s Advanced Photon Source.
refinement was performed by sequentially refining scale factor, zero point, background, lattice parameters, fractional coordinates, occupancies and atomic displacement parameters using the FullProf suite. Full details of the refinement results are presented in Table S1a–g.

## RESULTS AND DISCUSSION

The CuZr$_2$S$_4$ lattice was lithiated prior to cation extraction because previous studies have shown that, unlike CuTi$_2$S$_4$, no more than 70% of Cu can be removed from the Zr thiospinel topotactically through direct chemical oxidation. Since lithium can be removed using a mild oxidizing agent (e.g., I$_2$ in ACN), this preliminary ion exchange avoids the use of harsher oxidizers that simultaneously oxidize the sulfide lattice during the extraction process. After decopperiation, the resulting gray-brown powder consisted of primary crystallites ranging from approximately 0.3–1 μm in diameter (Figure S1), and the lattice parameter decreased from 10.3968(1) Å in pristine CuZr$_2$S$_4$ to 10.3561(2) Å in the oxidized material (Figure 1a,b). A combination of energy dispersive X-ray spectroscopy (EDX) and Rietveld refinement of X-ray diffraction (XRD) data (see Table 1) confirmed that the oxidized product maintained a spinel-phase cubic Fd$\bar{3}$m lattice and contained a minimal amount of residual copper, Cu$_{0.063(6)}$Zr$_2$S$_4$. Given the small Cu content, even though the lattice was not completely emptied, further references to the oxidized material are simplified to Zr$_2$S$_4$ for clarity and brevity.

Atomic resolution HAADF-STEM and ABF-STEM images show the spinel phase obtained after the removal of Cu from the lattice. Images of the oxidized Zr$_2$S$_4$ oriented along the [011] zone axis are also displayed in Figure 1, where projected atomic structures are superimposed onto the experimental images. In the HAADF-STEM image (Figure 1c) Zr columns are clearly visible and the ABF-STEM image (Figure 1d) elucidates S which has a lower atomic number.

The electrochemical behavior of Zr$_2$S$_4$∥Mg coin cells was measured at 60 °C. Figure 2a shows that the first and second cycles of these cells are markedly similar to those of Ti$_2$S$_4$∥Mg cells except that Zr$_2$S$_4$ has a lower average discharge potential of 0.76 V (compared to 1.18 V for Ti$_2$S$_4$). An irreversible capacity loss of about 20 mAh/g occurs after the first discharge, indicating some Mg$^{2+}$ is trapped within the thiospinel lattice (also visible in panels b and c). After the first cycle, Mg$^{2+}$ reversibly intercalates into the structure to give Mg$_{0.7}$Zr$_2$S$_4$ on discharge at a C/20 rate, corresponding to a capacity over 100 mAh/g. Compared to Mg$_{0.6}$Ti$_2$S$_4$∥Mg, Mg$_{0.7}$Zr$_2$S$_4$∥Mg cells
displays a much better Coulombic efficiency of 99.75(9)% for its first 50 cycles, as shown in Figure 2b. From cycle 50 to 70, soft short-circuits are evident in the galvanostatic potential profiles (Figure S2) until a complete, resistive, short-circuit is formed around cycle 70. These features in the electrochemical profile indicate the formation of Mg dendrites, as has been observed in previous studies. Several similar coin cells using one layer of glass fiber separator and either an all-phenyl complex (APC) or magnesium monocarborane (MMC) in tetraglyme (G4) electrolyte were cycled but all failed due to Mg dendrites. This emphasizes the need for future research to explore the conditions that support or eliminate Mg dendrite growth. Regardless of issues with the Mg negative electrode, thiospinel Zr\textsubscript{2}S\textsubscript{4} displays superior cycling stability which implies it has utility as a stable counter electrode to probe the properties of high voltage positive electrode materials in a rocking chair configuration. Employing Zr\textsubscript{2}S\textsubscript{4} as a counter electrode could facilitate the search for novel cathode materials by allowing the use of oxidation-resistant electrolytes that would otherwise passivate the surface of the traditional Mg negative electrode. 

Figure 2c shows the rate capability of a Zr\textsubscript{2}S\textsubscript{4}/MMC in G4/Mg cell cycled at 60 °C. About 70% of the capacity of Mg\textsubscript{x}Zr\textsubscript{2}S\textsubscript{4} at a C/20 rate is delivered at a C/5 rate. The fade rate depends on the cycling rate, as emphasized by the slope of the black linear fit drawn in Figure 2b. Because the fade rate is faster at slower cycling rates, the underlying mechanism is likely time dependent. A sustained chemical reaction may occur that slowly degrades the Zr\textsubscript{2}S\textsubscript{4}, which might be the breakdown of intercalated MgZr\textsubscript{2}S\textsubscript{4} into MgS and transition metal sulfides. Figure 2d illustrates the differential capacity (dQ/dV) of a typical cycle at C/50. The broad peak at higher potential indicates a single phase process, such as intercalation. The valley between the broad and narrow peaks, at about 0.77 V during discharge, could be due to Mg\textsuperscript{2+} ordering (i.e., when the octahedral 16c sites are 1/4 filled) as postulated by Emly and Van der Ven in the Mg\textsubscript{x}Ti\textsubscript{2}S\textsubscript{4} thiospinel; however, XRD evidence of ordering was not observed for either the Ti\textsubscript{2}S\textsubscript{4} or Zr\textsubscript{2}S\textsubscript{4} thiospinels in our work. In fact, the sharp peak at lower potentials in Figure 2d is commonly indicative of a two-phase reaction, suggesting the valley is instead a transition from one electrochemical process to another as described below.

The reversible intercalation of Mg\textsuperscript{2+} on cycling was confirmed using a combination of EDX, XRD, and Rietveld refinement at various states of (dis)charge (i.e., Mg\textsubscript{x}Zr\textsubscript{2}S\textsubscript{4}, 0 ≤ x ≤ 1), as summarized in Table 1. Because the Cu content in electrochemically cycled materials was invariant within...
Zr L2-, Zr L3-, and S K-edges EELS spectra for the pristine (chemical Mg2+ content calculated assuming two electrons per and EDX measurements were comparable to the electro-
materials, accompanied by the lower L3/L2 ratio, indicates a edges toward higher energy (2228 eV) in the discharged pristine material. The peak energy of the charged material shifts back to lower energy (2225 eV), similar to that of the discharged materials and almost completely disappears after charging. The remaining intensity of the Mg K-edge peak is due to residual Mg2+ in the structure. The shift of the Zr L2,3- edges toward higher energy (2228 eV) in the discharged materials, accompanied by the lower L3/L2 ratio, indicates a lower average oxidation state of Zr in comparison to the pristine material. The peak energy of the charged material shifts back to lower energy (~2225 eV), similar to that of the pristine material (2224 eV). In contrast, the peak position and fine structure of the S K-edge is almost identical in all four materials indicating that S is electrochemically inactive throughout (dis)charge. This correlates well with sulfur 2p XPS data that compares charged and discharged MgZr2S4, which also reveals no S redox activity (Figure S5). To further confirm the intercalation of Mg2+, MgZr2S4 was discharged to x = 0.6 was explored with STEM. Of the six different octahedral Mg2+ sites in the structure, two do not overlap with Zr atoms along the [011] projection axis, and thus their presence can be used to verify Mg2+ occupation. The multislice HAADF-STEM image simulation performed on Mg0.67Zr2S4 (top-left inset in Figure 3d) clearly shows the columns of octahedrally coordinated Mg2+ ions in the ABF-STEM image along this zone axis. The contrast observed in the experimental ABF-STEM image matches the simulation well, and the Mg ion columns are highlighted by the red boxes in Figure 3d.

To further investigate Mg2+ insertion into the Zr2S4 structure, we analyzed MgZr2S4 discharged to x = 0.4 and x = 0.6 with electron energy loss spectroscopy (EELS) and atomic resolution STEM. Figures 3a and b display the Mg K-, Zr L2,3-, Zr L1, and S K-edges EELS spectra for the pristine (x = 0), discharged (x = 0.4 and 0.6) and recharged (x = 0.1) materials. The Mg K-edge peak at 1300 eV appears in the discharged materials and almost completely disappears after charging. The remaining intensity of the Mg K-edge peak is due to residual Mg2+ in the structure. The shift of the Zr L2,3- edges toward higher energy (2228 eV) in the discharged materials, accompanied by the lower L3/L2 ratio, indicates a lower average oxidation state of Zr in comparison to the pristine material. The peak energy of the charged material shifts back to lower energy (~2225 eV), similar to that of the pristine material (2224 eV). In contrast, the peak position and fine structure of the S K-edge is almost identical in all four materials indicating that S is electrochemically inactive throughout (dis)charge. This correlates well with sulfur 2p XPS data that compares charged and discharged MgZr2S4, which also reveals no S redox activity (Figure S5). To further confirm the intercalation of Mg2+, MgZr2S4 was discharged to x = 0.6 was explored with STEM. Of the six different octahedral Mg2+ sites in the structure, two do not overlap with Zr atoms along the [011] projection axis, and thus their presence can be used to verify Mg2+ occupation. The multislice HAADF-STEM image simulation performed on Mg0.67Zr2S4 (top-left inset in Figure 3d) clearly shows the columns of octahedrally coordinated Mg2+ ions in the ABF-STEM image along this zone axis. The contrast observed in the experimental ABF-STEM image matches the simulation well, and the Mg ion columns are highlighted by the red boxes in Figure 3d.

X-ray absorption spectroscopy (XAS) confirms that Zr4+ is reduced to a formal oxidation state of Zr3+ during discharge and oxidized during charge. However, in a highly covalent lattice, zirconium’s “true” oxidation state will not be equivalent to its formal value. Figure 4a shows the Zr K-edge (XANES) for MgCuZr2S4 at various states of x and y, while panel b shows a magnified image highlighting the energy values at half-height of the normalized XANES spectra (E0.5, circles). Zr undergoes reversible redox when Cu ions are removed from the CuZr2S4 thiospinel (gray to black curve), and as Mg2+ is inserted (black to red curve) and removed (red to blue curve). Surprisingly, the E0.5 energy of discharged
Mg$_{0.76}$Cu$_{0.08}$Zr$_2$S$_4$ is higher than pristine CuZr$_2$S$_4$ in Figure 4b, which is not consistent with the commonly assumed oxidation state of +1 for Cu in thiospinels. A comparison between the differences in $E_{\text{ox}}$ values and the Mg and Cu compositions, as measured by EDX, reveals that the Zr K-edge energies are only consistent if Cu is in a +2 oxidation state (see Table S2). Unfortunately, Cu K-edge XANES experiments comparing Cu$_2$S, CuS and CuZr$_2$S$_4$ were inconclusive in directly measuring the copper oxidation state (Figure S6) because of the differing local structure and bonding in these compounds (Table S3).43,44

The local structure of zirconium and copper in Mg$_{0.76}$Cu$_{0.08}$Zr$_2$S$_4$ was also probed by EXAFS. The main results of the fits to the EXAFS data are given in Table 2; further details can be found in the SI (Figure S7). When copper is removed from CuZr$_2$S$_4$ to form ZrS$_4$, there is a small but measurable decrease in the Zr–S correlation distance by $\sim0.015$ Å. Likewise, the Zr–Zr correlation distance also decreases by $\sim0.028$ Å. These observations are consistent with the changes expected upon zirconium oxidation. When Mg$_{2+}$ is inserted to form Mg$_{0.76}$Zr$_2$S$_4$, the Zr–S bond distance recovers to a value close to that seen for CuZr$_2$S$_4$. This is consistent with the reduction of zirconium on magnesium insertion. Intriguingly, the Zr–Zr correlation distance decreases slightly or remains similar to ZrS$_4$ within the uncertainty of the measurements. On subsequent removal of Mg$_{2+}$, the Zr–S bond distance returns to a value similar to that seen for ZrS$_4$, consistent with the oxidation of zirconium. However, again the Zr–Zr correlation distance remains largely invariant. The variations in the Zr–S bond distances after discharge/recharge prove that the redox charge compensation is endured by zirconium, in agreement with the XANES and EELS results. The absence of significant changes in the Zr–Zr correlation distance also confirms that the system behaves as a zero-strain material, even on the medium-range scale. This echoes the beneficial behavior seen in the XRD data (vide infra), which elucidates the response of the average structure.

Figure 5. Operando XRD performed during cycling of a Mg$_{0.76}$Zr$_2$S$_4$/APC in G4Mg at 60 °C and a C/20 rate. (a) Sequential XRD patterns from the cell. Every other scan recorded is shown, corresponding to $\Delta x \sim 0.05$ in Mg$_{0.76}$Zr$_2$S$_4$. (b) Cubic Fd$ar{3}$m cell parameter evolution as a function of x. Phase 1 (blue squares) shows minimal lattice strain and Phase 2 (red circles) appears around $x \sim 0.5$ during discharge. (c) Cell voltage of the first cycle as a function of x.

Operando XRD studies were performed on a Zr$_2$S$_4$/Mg cell to better characterize the structural changes taking place within the Mg$_{0.76}$Zr$_2$S$_4$ lattice during each stage of discharge. The results are shown in Figure 5a, which depicts the (004) and (044) reflections that are characteristic of the appearance and disappearance of a second Fd$ar{3}$m phase at $x \geq 0.5$, as suggested by the dQ/dV plot (Figure 2d). Le Bail fitting was used to track the lattice parameter evolution of the spinel phase(s) upon Mg$_{2+}$ (de)intercalation (Figure 5b). During the first half of discharge, the lattice parameter does not deviate significantly from its pristine value, indicating a zero-strain lattice as Mg$_{2+}$ enters the structure up to $x \sim 0.5$. After this point, the material splits into two separate cubic Fd$ar{3}$m phases where Phase 1 (blue squares) maintains a relatively static lattice parameter and Phase 2 (red circles) exhibits a slight increase. The single phase material is recovered on subsequent recharge as Mg$_{2+}$ exits the lattice. Since strain-induced cracking promotes continual SEI growth, and eventually leads to pulverization, prohibiting this source of capacity fade would further optimize electrochemical performance. As such, the lack of significant strain during cycling in Mg$_{0.76}$Zr$_2$S$_4$ likely contributes to the good Coulombic efficiencies displayed in Figure 2b.

The galvanic intermittent titration technique (GITT) was used to compare the Mg$_{2+}$ diffusivity between the analogous thiospinels Mg$_{0.76}$Zr$_2$S$_4$ and Mg$_{0.76}$Ti$_2$S$_4$ (Figure S8).33 Figure 6 shows that there is a sharp decrease in the Mg$_{2+}$ diffusion coefficient during the discharge of Mg$_{0.76}$Zr$_2$S$_4$ that is coincident with the onset of phase separation. In this two phase regime, the standard GITT technique cannot accurately determine D$_{\text{Mg}}$ and thus we denote data for D$_{\text{Mg}}$ for $x > 0.5$ as a dotted line. Interested readers are directed to the work of Zhu and Wang, who propose a technique to deconvolute the ion diffusion and phase boundary movement in two phase regimes.35 Their phase transformation GITT method has shown that the true ion diffusion coefficient in two-phase regions can be several orders of magnitude higher than what is predicted by standard GITT experiments. This suggests that
$D_{\text{Mg}}$ in Mg$_x$Zr$_2$S$_4$ may not decrease as sharply beyond $x \sim 0.5$ as indicated in Figure 6. Further investigation is required to elucidate the true behavior in this region, which is outside the scope of this work. Thiole et al. have suggested that intercalation diffusion rates are also dependent on the ease with which the electron cloud in the host can travel through the lattice to accompany the moving cation, but theory reveals that in the metallic Chevrel phase, the ionic charges of the sulfide anions are shielded from the highly charged Mg$^{2+}$ ion by the itinerant electrons of the framework. Consistent with this finding is the fact that our measurements show that Zr$_2$S$_4$ ($\sigma_e = 1.7 \times 10^{-4}$ S/cm) is much less electronically conductive than Ti$_2$S$_4$ ($\sigma_e = 3.54$ S/cm). The lower electronic conductivity of CuZr$_2$S$_4$ vs CuTi$_2$S$_4$ has also been reported in the literature, and is ascribed to a difference in band structure. We conclude this factor is responsible for the more sluggish Mg$^{2+}$ diffusion in the poor semiconductor Zr$_2$S$_4$, indeed showing that the diffusivity of divalent ions is very sensitive to the degree of electron delocalization in the lattice.

Ex situ synchrotron XRD (Figure 7) also demonstrates that the thiospinel maintains the cubic $Fd\bar{3}m$ space group on Cu-ion extraction and throughout Mg$^{2+}$ cycling as expected, and the structural data obtained from Rietveld refinement are in good agreement with the EXAFS results (Table S4). These structural data were used to confirm that an equally facile diffusion pathway is available in the larger Zr$_2$S$_4$ lattice in comparison to Ti$_2$S$_4$. Because the bottleneck to Mg$^{2+}$ diffusion in the thiospinel lattice is the migration through the triangular face shared between adjacent octahedral and tetrahedral sites, the bond distance between a Mg$^{2+}$ ion in the center of this face and its closest S neighbor was calculated. This distance is even longer in Zr$_2$S$_4$ (2.149(4) Å) than in Ti$_2$S$_4$ (2.089(3) Å), confirming that the limited Mg$^{2+}$ diffusivity...
observed in Figure 5 is not due to a more restricted window in the Zr thiospinel lattice. In Figure 7, the slight decrease in lattice parameter upon oxidation from CuZr2S4 to Zr2S4 signifies that the lattice shrinks as Cu2+ is removed from the tetrahedral (8a) lattice sites. Rietveld refinement reveals that MgZr2S4 exhibits minimal (almost zero) strain throughout the first half of discharge as described above in Figure 5, during which Mg2+ only occupies octahedral (16c) sites. The larger phase forms in the second half of discharge when Mg2+ begins occupying tetrahedral (8a) sites as well (Figures S3 and S4, and Table S1a–f). Since the Zr thiospinel lattice is only forced to expand during the latter step, the tetrahedral site occupancy results in an increase in cell volume and separation of a second Fd3m phase observed in the operando XRD studies shown in Figure 5.

The experiments shown in Figure 7 demonstrate that as MgZr2S4 is discharged, Mg2+ ions occupy thermodynamically favored octahedral sites47 from x = 0 to about 0.5, as they migrate toward the core of the particle. The sharp onset of dual phases that clearly form during discharge in equilibrated material in panel b was left in the cell at 60 \degree C until d cell = 0.1 V. If a C/20 discharged electrode is equilibrated for several days before disassembly (until dV/dt drops below 0.1 mV/h), then the ratio of Phase 1:Phase 2 in Mg0.7Zr2S4 increases over time, from 43:57 in nonequilibrated electrodes to 55:45 in equilibrated electrodes (Figure 8a vs 8b, and Table S1e). In all C/20 discharged phases, the fraction of Mg2+ occupying octahedral sites is capped below a maximum of x = 0.6, near the sharp decrease of Mg2+ diffusivity in the Mg,Zr,S4 lattice (Figure 6, Table S1d,e). The total Mg2+ content can be pushed beyond x = 0.7 by discharging the material using slow rates at 60 °C. MgZr2S4 discharged at C/40 and C/100 reached final compositions of Mg0.88Zr2S4 and Mg0.9,Zr2S4, respectively (Figure 8c, d). In these cases, the discharged material mostly comprised Phase 2 (Mg[oct]0.5,Mg[tet]0.4Zr,S4), because the larger lattice forms at high Mg2+ occupancy (Figure 5). Interestingly, the composition of Phase 1 remaining in these materials showed a significant increase in octahedral site occupation up to Mg[oct]0.5Zr2S4 in the sample discharged at C/100 (Table S1e). This indicates that pushing octahedral occupation beyond x = 0.5 is thermodynamically achievable, yet kinetically inaccessible at reasonable discharge rates.

### CONCLUSIONS

Synthesis and examination of the new zero-strain Mg2+ intercalation material, thiospinel MgZr2S4, provides important insight into the factors that control Mg2+ intercalation and diffusion within solid lattice structures. Electrochemical, HAADF-STEM, EDX and XRD Rietveld refinement of compositions at various states of charge provide clear evidence of Mg2+ insertion in this material, which exhibits an impressive Coulombic efficiency of 99.7% because of its mostly static lattice parameters during cycling. During the initial stages of discharge (x > 0.5), Mg2+ only occupies octahedral (16c) sites, but on deeper discharge Mg2+ ions begin occupying tetrahedral (8a) sites in MgZr2S4 at about x = 0.5. Tetrahedral site occupation presumably begins as the energy of the tetrahedral and octahedral sites become equivalent; however, we cannot rule out the role that kinetics may play in determining the average Mg2+ concentration at which this occurs. Tetrahedral site occupation expands the lattice, triggering a phase separation between the zero-strain core where Mg2+ occupies only octahedral sites, and the expanding shell where Mg2+ occupies both octahedral and tetrahedral sites. This process is an example of two thermodynamically distinct solid solutions where the crossover between phases is driven by local volume changes.

More importantly, comparison of the two nearly isostructural materials, Mg,Ti2S4 and Mg,Zr2S4, allows the identification of factors controlling ion diffusivity. We find that the electrical conductivity of the host material is a crucial factor in determining magnesium ion diffusivity. This is evidenced by the much lower Mg2+ diffusivity of Mg,Zr2S4, despite exhibiting a zero-strain lattice and slightly larger unit cell volume, in comparison with Mg,Ti2S4, which has an electrical conductivity 4 orders of magnitude higher. This also highlights the challenge in developing purely insulating solid electrolytes for use with divalent cations.49 In the ongoing search for new Mg-ion positive electrode materials, targeting mixed ion/electronic conductors that exhibit high electronic conductivity of the host is important to unlock a boost in Mg2+ diffusion rates.

**Figure 8.** Summary of the Rietveld refinement site occupancy data for MgZr2S4 discharged at different rates (see Tables S1d, e). The equilibrated material in panel b was left in the cell at 60 °C at open circuit until dV/dt <0.1 mV/h; the other materials were analyzed by XRD immediately after discharge finished at E = 0.1 V.
Further discussion of phase separation, detailed experimental methods, Rietveld refinement methods and results, XANES analysis of Cu oxidation state, EXAFS details (including the raw EXAFS spectra, Fourier transforms and a comparison of the raw data to the fits), SEM images, demonstration of soft short-circuits in electrochemical cycling, sulfur 2p XPS, raw data for the GITT experiments (PDF)

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Authors Contribution

P.B. and L.F.N. conceived the experiments and study; P.B. and L.B. carried out the materials synthesis, electrochemical studies, and materials characterization/analysis with the help of X.S. S.H.V. performed the synchrotron XRD experiments. Electron Microscopy work was carried out at the Canadian Centre for Electron Microscopy (CCEM), a facility supported by NSERC and McMaster University. P.B. also thanks Dr. Jung-Soo Kang for his help with XPS.

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