The Synthesis of Magnesium Metal-Organic Framework Film for Ion Transport in Magnesium Battery

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Abstract

Metal organic frameworks (MOFs) are a class of compounds that show promising potential for a variety of applications due to their uniformity, highly porous structure, lack of dead volume, and fine-tunability. One of these significant applications is in selective ion transport, which makes MOF films a uniquely good separatory material for dual-electrolyte setups, such as those being investigated with Mg-Br batteries. This research has important environmental and industrial ramifications, considering the various drawbacks associated with commercially available batteries such as the lithium-ion battery. The MOF investigated was Mg-MOF-74, which showed promising selective Mg²⁺ transport abilities. Both Mg-MOF-74 powder and films were synthesized via a vapor-assisted conversion process to maximize efficiency. To characterize the MOF, XRD and SEM imaging was used. This allowed us to gain a nuanced understanding of the material and its properties for further applications.

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I. Introduction

One area of chemistry that has gained a significant amount of attention in recent years has been that which aims to develop the next generation of electrochemical energy storage technologies, from both industrial and environmental perspectives. As we understand more about clean energy storage and consumption, it becomes pertinent to develop energy storage mechanisms that are both environmentally-conscious and sustainable. Batteries are at the forefront of this research, considering the widespread usage and everyday applications. This paper first outlines the current approaches to batteries, their relevant issues, and gives a brief overview of the general work being done to investigate new possible options. Then, an overview of the specific research project is given, presenting details on the magnesium battery and Mg-MOF-74 being researched, in order to provide sufficient context for the upcoming syntheses and characterizations.

II. Lithium-Ion Battery Background

To understand the scope of the issue, as well as the significance of the research being done, it is important to understand both the lithium-ion battery and the issues with it and the magnesium battery as it is being studied as a replacement. The lithium-ion battery is widely used in consumer electronics, including mobile phones and laptop computers, as well as automobiles and industrial energy storage systems. These batteries were introduced to the market in 1991, and have been increasingly used since. Not only were they developed at the right time to grow in popularity as technological products grew in popularity, but lithium-ion batteries show excellent performance as well, adding to their utility. These batteries have a high specific energy and energy density, and are incredibly efficient and long-lasting. A lithium-ion battery consists of a positive cathode, generally composed of lithium oxide, and a negative anode, generally composed of a carbon material or metal oxide. During the charging process, the cathode releases Li ions, which flow to the anode; in the discharging process, the Li ions flow from the anode to the cathode.¹

While this battery is, as mentioned, highly effective and widely used, there are a number of issues involved. Firstly, there are safety concerns. Lithium-ion batteries are prone to dendrite growth when lithium ions accumulate on the anode surface and cannot be reabsorbed properly. These dendrites can degrade the battery and short-circuit and catch fire, leading to safety hazards.² Furthermore, lithium-ion batteries usually use organic electrolytes consisting of aprotic polar organic solvents and a lithium salt; this electrolyte is highly combustible and thus further poses a safety concern.¹ Lithium is also a relatively scarce element, and thus there are economic disadvantages to a battery that requires it in abundance.³ Finally, there is a demand for higher capacity energy storage than lithium-ion batteries can keep up with, with particular focus towards rechargeable batteries, which improve energy density by using metal anodes.⁴

III. Magnesium Battery Developments

One such battery that is being widely studied is the magnesium battery, which offers a variety of advantages as compared to a lithium-ion battery. Magnesium is a relatively abundant element—the fifth most abundant on the Earth's crust, in fact.⁵ This natural high supply of the element is about 300 times greater than that of lithium, making magnesium both a much lower-cost option, and more environmentally friendly.⁶ Additionally, the use of a magnesium metal anode addresses many of the safety concerns associated with lithium-ion batteries, as the magnesium anode exhibits negligible amounts of dendrite growth, if any.³ Furthermore,

magnesium batteries have been shown to be highly efficient. Magnesium shows a volumetric capacity of 3832 mAh cm⁻³, as compared to 777 mAh cm⁻³ for commercialized lithium-ion battery graphite anodes, or 2046 mAh cm⁻³ for lithium itself.^{6,5} As such, magnesium batteries have greater volumetric densities, and are well-suited for applications where small size is favorable, such as portable electronics.⁴

However, despite their theoretical superiority, there remain a number of issues to be resolved before magnesium batteries can replace lithium-ion batteries in practical applications. The largest of these issues involves the electrolyte used in the battery; this issue was briefly mentioned in the description of the research project. The electrolyte(s) commonly used for lithium-ion batteries do not work for magnesium batteries—a passivation layer forms on the surface of the magnesium anode as the electrolyte species reduces, making the anode electrochemically inactive.⁶ Furthermore, Mg²⁺ has poor mobility and slow insertion kinetics in solid-state electrolytes, and there is yet no known solution-based electrolyte that can both facilitate the conversion reaction at the cathode while not interfering with the stripping/plating occurring at the anode.³ As is the case with this project, one approach to solving this issue is to employ separate electrolytes for the anode and the cathode. This is the case with a proposed magnesium-bromide battery, which converts between Mg and Br₂, utilizing different electrolytes for the two reactions.⁵

IV. Use of MOFs for Ion Transport in Mg-Battery

In order to tackle the issues surrounding lithium-ion batteries and develop a suitable replacement battery, the aforementioned intricacies of a magnesium battery must be studied in detail. This metal-organic framework (MOF) synthesis project was completed in the context of a

larger research project; to understand the implications of the work done it is necessary to understand the context of the larger project and its goals. This project, as described in the initial proposal, tests that "fast and selective transport of multivalent ions through MOF-based materials can be achieved through tuning the structural components."⁷ On a grander scale, the project focuses on replacing lithium-ion batteries with a more sustainable, economic, safer option. In this sense, magnesium materials are focused on, including Mg-S, Mg-O₂, and Mg-Br batteries.⁷ However, the main issue with this exploration, as this project is neither the first nor only one to conceptualize a magnesium battery, is that the electrolyte used in a lithium-ion battery is not compatible with the magnesium battery; furthermore, the electrolytes that would work well with the conversion-chemistry on the cathode side are generally not compatible with the magnesium stripping and plating chemistries on the anode side of the battery. As such, a dual-electrolyte system is examined, where the anode and cathode reactions each are submersed in their own compatible electrolyte. To that end, the need for a separator arises to block the exchange of electrolytes, with the caveat that the separatory material must allow for the transport of Mg²⁺ ions in order for the reaction to proceed.³ As will be discussed in detail shortly, MOFs have shown excellent fast and selective ion transport abilities, making MOF thin films the material of choice for the separator. As previously mentioned, the fine-tunability of MOFs make them suitable for this application, allowing the interactions between ions and structural components of the framework to be optimized for effective and efficient ion transport and electrolyte blockage.⁷

Existing studies have already demonstrated that MOF films, specifically Mg-MOF-74 thin films, can be synthesized on a variety of substrates to transport Mg^{2+} ions. Mg-MOF-74 as a choice of MOF will be discussed in greater detail shortly. Further studies have also shown that these same films can simultaneously effectively block solvents and undesired anions from

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crossing the film.⁸ These two aspects of the MOF film are vital to its usage as a separator in a magnesium battery, where it must facilitate the transport of Mg²⁺ ions without allowing the cross-transfer of anolyte and catholyte. Thus, there is existing research to support the work of this project and its viability.

V. Metal Organic Frameworks

In order to understand the focus of this project, it is important to understand what MOFs are, their common applications, and how they function. MOFs are a class of porous materials that are quickly rising in popularity in the scientific community, for their multitude of applications that will be explored shortly. They consist of metal nodes coordinated to organic linkers with strong bonds via reticular synthesis.⁹ MOF films have been synthesized via a reaction between a metal-containing precursor layer and a liquid organic linker; the synthesis of MOFs will be explored in greater depth further on.¹⁰ MOFs are formed in repeating geometric patterns, forming cage-like structures with open channels. These open channels create permanent porosity. These structures can be one, two, or three dimensional, depending on the specific coordination of the metal-containing unit. This results in an open crystalline framework, lending MOFs their name.⁹ Figure 1 below shows a variety of different MOF structures, highlighting an non-exhaustive set of the different conformations that are possible—all geometric, repetitive, and uniform. These are key characteristics of MOFs.



Figure 1. Illustration of a variety of MOF structures. Reprinted with permission from Ref.¹¹ Copyright 2020 American Chemical Society.

MOFs have a variety of unique features that enable them to be used in so many different applications. MOFs have a high degree of chemical and structural tunability: one can vary both the metal and organic components used to create the MOF with great flexibility.¹² This allows for very specific intentionality in the composition of the MOF, allowing one to tailor it to the specific intended purpose. For example, a particular metal ion can be used in the metal node in order to bind to particular ions, making that MOF suitable for separating and transporting said ions. Furthermore, this adjustment to the chemical structure of the MOF can mitigate the interaction of ions with their chemical environment, therefore adjusting the conductivity of the material.² This flexibility in composition additionally allows for nearly endless combinations of organic-inorganic linkers;⁹ as a result, there are constantly discoveries being made with new MOFs—over 1000 publications on "metal–organic frameworks" and "coordination polymers" are being published every year.¹³

Additionally, the impressive porosity exhibited by MOFs contribute to their usefulness. Studies have shown that MOF structures have a total lack of non-accessible bulk volume; this lack of dead volume leads to exceptionally high surface areas and porosities.¹³ For example, it was reported that MOF-177 has a surface area of up to 5640 m² g⁻¹, and MIL-101 has a surface area of up to 5900 m² g⁻¹.^{14,15} This property allows for easy access to the channels in the porous material, making MOFs practically useful. The pores are not only controllable in size, but regularly distributed throughout the material, given the geometric patterned structure. These open channels are an important aspect of MOFs, as they allow for the passage of different molecules through the MOF. These structures are additionally known to have high thermal and mechanical stability due to their repeating units in the solid form and coordination of metal ions.¹³

VI. Applications of MOFs

As mentioned previously, MOFs are gaining popularity in the chemical industry and research due to their wide variety of potential applications. It is worth exploring a number of these applications to understand the ways in which these materials can be utilized.

One of the most promising, and most important, applications for MOFs lies in their ability to quickly and selectively transport ions. Firstly, MOFs have an inherently crystalline and porous nature to the material; this provides closely-spaced binding sites for ions, allowing them to move quickly within the open framework, lending good ionic conductivity to MOF materials. Furthermore, the previously-described metal node and organic linker structure of MOFs is highly fine-tunable, due to the rich selection of possible nodes and linkers. Additionally, the variation of components can allow one to select pore size and shape as well;²⁸ thus, not only can the components be functionalized to optimize ion transport selectivity and speed, but to limit the transport of unwanted species as well.¹ The inherent porosity and uniform pore size of the material creates ion channels by which ions such as H⁺, Na⁺, K⁺, etc, can be transported due to their similarities to natural ion channels. Additionally, these channels can act as selective membranes, either via the unsaturated metal sites or functional groups, to control the interactions between the ions entering the channel and the MOF framework, further keeping out unwanted species.¹⁶ For example, one study proved that in a battery context, Mg-MOF-74 film was an effective separator, as it successfully blocked the solvents and anions from crossing over between the different electrolytes.³ This will be discussed later as highly relevant to the ongoing project. Figure 2 below illustrates, very simply, the mechanism by which MOFs can act as ion-selective membranes. The target ions are able to pass through the porous channels in the MOF, while the

undesired molecules—in the figure below, the cations and anions—do not fit into the channels and are thus blocked by the membrane, bouncing back.



Figure 2. Illustration of the selective ion-transport mechanism in MOF membranes. Reproduced with permission from Ref.¹⁶Copyright 2021 John Wiley and Sons.

MOFs are also promising candidates for gas storage, separation, and purification. In regards to gas purification, one study showed that MOFs show promising results when used to remove ppm-level traces of sulfur components from a variety of gasses. This is because the open metal sites on MOFs can chemically adsorb electron rich molecules such as amines, phosphines, and sulfur-based molecules.¹³ Additionally, MOFs are well-suited for gas storage applications thanks largely to their lack of dead volume; which ensures that the MOF itself does not occupy space otherwise used for gas storage, increasing the storage capacity. MOF-filled gas cylinders, for example, not only store gas in the cylinder itself, but adsorbed in the MOF framework as well.¹³

Thus, in such examples it is possible to store a greater volumetric amount of gas than expected. This application specifically presents an exciting possibility for hydrogen storage, to be used as fuel. MOF storage of hydrogen has been shown to be completely reversible and relatively simple.¹⁷

Furthermore, MOFs make excellent catalyst materials, the reasons for which are similar to the reasons why MOFs are useful in other applications as well. The structure of MOFs, which has been previously described in greater detail, contains open metal sites arranged in a regular pattern, with little dead volume, and a high surface area—this leads to a high density of exposed sites for catalysis in a given volume of MOF, making the material more catalytically active. Furthermore, the highly tunable nature of MOFs enable them to be easily molded into the ideal catalyst. Not only can the identity of the nodes and linkers be modified as needed, but so can the pore size and shape to further increase selectivity and efficiency of the catalyst.¹³ Additionally, beyond using the open sites on the MOF framework, to use it to support an existing catalyst.¹⁸

There has additionally been research done to explore MOFs as alternatives for bioenzymes. MOF-based nanozymes are a type of artificial enzyme, composed of MOF nanomaterials that exhibit enzyme-like characteristics.¹⁹ These materials make suitable bioenzyme alternatives due to their impressive sensing and detecting capabilities, which stem from the high porosities. In this regard, colorimetric and optical sensing have been utilized; this has been shown to be applicable to both sensing organic species and detecting inorganic species.¹⁸

It is quickly becoming apparent that MOFs are a class of materials that hold an exceptional amount of potential, for applications that vary vastly. There are a great number of

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further applications that have not been discussed, including: drug delivery,²⁰ microelectronics,¹⁰ supercapacitors,²¹ pollution control,²² and optic sensors.²³

VII. Mg-MOF-74

It is additionally worth examining closer the specific MOF being investigated and synthesized in this project: Mg-MOF-74. Mg-MOF-74, also sometimes referred to as CPO-27,²⁴ is composed of Mg metal nodes and 2,5-dihydroxyterephthalic acid, also sometimes referred to as 2,5-dihydroxy-1,4-benzenedicarboxylic acid, linkers.² These nodes and linkers are arranged hexagonally in a honeycomb-like a one-dimensional layer, creating large porous channels, the openings of which are approximately 13 Å in size.^{25,1} Figure 3 below shows a visual representation of Mg-MOF-74, with two slightly different orientations to demonstrate its full hexagonal, cage-like structure. Two repeating units of the MOF are shown, though it is important to note that these two alone do not represent the whole framework, which extends on all sides. In Figure 3, Mg atoms are shown in orange, oxygen atoms in red, carbon atoms in brown, and hydrogen atoms in light pink. The models were created using the VESTA software; the cif file was obtained from The Cambridge Crystallographic Data Centre.²⁶



Figure 3. Ball-and-stick model representation of two repeating units of Mg-MOF-74. (a) Top-down view. (b) Angled view.

In this hexagonal configuration, each Mg atom coordinates with three O atoms from the carboxylate and two O atoms from the hydroxy group. The sixth coordination site on the Mg is occupied by the solvent molecule, which can be removed by heating or vacuum treating the material, resulting in an open metal site.²⁵ In this synthesis, the solvent used is dimethylformamide (DMF), which originally coordinates to the empty Mg site, but is removed upon activation, resulting in Lewis acidic open metal sites.²⁴ These open metal sites are one of the reasons why Mg-MOF-74 is such an effective material for ion transport. Adjacent open metal sites are ~3 Å apart, allowing molecules to not only bind to individual open metal sites, but to quickly hop between successive sites as well. This particular property allows the material to transport Mg²⁺ efficiently.¹ Generally, these open metal sites can bind most nucleophilic species, making Mg-MOF-74 a highly useful material.³ Furthermore, the material has a relatively high density of open metal sites, high porosity, large surface area, and high ionic conductivity, making it further useful for a variety of applications, especially but not exclusively ion transport.^{24,3}

For a full understanding of this specific material, it is worth examining in greater detail the binding and transport mechanism of Mg^{2+} in Mg-MOF-74. One study found that inside the MOF, Mg^{2+} exhibits binding not only to the open metal site, but to solvent molecules as well. It was found that different solvation states coexist at equilibrium in the MOF framework. Mg^{2+} was placed inside a MOF pore along with three dimethoxyethane (DME) molecules; three solvated states were found. $[Mg(DME)_3]^{2+}$, wherein Mg^{2+} is fully solvated, was found alongside $[Mg(DME)_2]^{2+}$ and $[Mg(DME)]^{2+}$, wherein Mg^{2+} is partially solvated.

Furthermore, it was observed that there are two possible methods for Mg^{2+} to bind to the MOF: it either binds directly to the MOF surface via adsorption onto one of the oxygen atoms of the carboxylate group of the 2,5-dihydroxyterephthalic acid linker, or the Mg ion gets solvated in

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some capacity, and the solvent molecule binds to the open metal site on the MOF.³ Figure 4 below shows these two binding sites: Figure 4(a) shows the latter, where $[Mg(DME)_2]^{2+}$ is bound to a Mg atom in the MOF via a bridge DME molecule; Figure 4(b) shows the former, where the $[Mg(DME)_2]^{2+}$ is bound to the MOF directly.



Figure 4. Graphic representation of the binding sites for Mg ions in Mg-MOF-74. Adapted with permission from Ref.³ Copyright 2021 American Chemical Society.

Finally, investigation of the Mg²⁺ transport mechanism found that each of the two aforementioned potential binding methods had their own potential movement method associated with it. The Mg²⁺ could either move via "linker hopping," where it moved from the carboxylate oxygen of one MOF linker to the carboxylate oxygen of the next linker, or via "solvent hopping," where it moved from one bridge solvent molecule to another. It was determined that solvent hopping had the lower energy barrier, making it the more probable and accessible mechanism.³ While the DME solvent is different from the DMF used in this experiment, the findings can nevertheless be extended to understand the behavior of the Mg-MOF-74 being synthesized.

VIII. Synthesis And Characterizations

The MOF films were synthesized via a vapor-assisted conversion method. This method generally involves laying down a layer of metal-containing MOF precursor solution onto a substrate; high vapor pressure from surrounding solvent prevents evaporation of the precursor solution, allowing for successful film growth.¹ This method has a number of advantages over other solution-based methods: it uses less organic solvents, limits film deposition strictly to the substrate surface, allows one to exert greater control over the film thickness, and results in more uniform films.¹⁰

Figure 5 below shows a simple representation of the vapor-assisted conversion synthesis process. In this, one can observe the presence of a precursor solution on a substrate as well as a source of vapor in a sealed vessel, which leads to film growth as it is heated. This general procedure guides the following synthesis of Mg-MOF-74.



Figure 5. Illustration of the vapor-assisted conversion method synthesis of Mg-MOF-74. Reprinted with permission from Ref.²⁷ Copyright 2021 American Chemical Society.

Mg-MOF-74 particles were first synthesized in order to practice and understand the synthesis process. First, 120 mg of 2,5-dihydroxyterephthalic acid (H₄DOT) were combined with 33 mL of dimethylformamide (DMF) and 171.6 μ L of acetic acid (HOAC). Separately, 1.3846 g of magnesium nitrate (Mg(NO₃)₂) were combined with 9.426 mL of DMF and 3.537 mL of ethanol. The Mg(NO₃)₂ solution was added to the H₄DOT solution. Then, 3.537 mL of 1.23 M sodium hydroxide (NaOH) was added slowly to the solution while stirring and watching for precipitate formation. The solution was heated at 100°C for 24 hours. The newly-created MOF particles were washed three times through centrifuging with DMF, then three times with methanol. After the second methanol centrifuge, the solid particles were collected in a vial and then centrifuged again. The Mg-MOF-74 particles were then activated in a vacuum oven overnight to remove solvent molecules from the binding sites on the framework. This resulted in a light yellow, chalky powder. A photo of the MOF particles is shown in the Appendix. It is worth noting that this photo was taken after a significant waiting period—the powder was initially less clumped.

X-ray diffraction (XRD) was used to analyze the MOF particles. XRD measures the intensities and scattering angles of x-rays that leave a material; the interference of the crystal structure of the material affects the distribution of scattering, thus giving insight into the composition of the material being studied.

Figure 6 shows a simulated XRD spectrum for Mg-MOF-74 particles. The powder diffraction pattern was simulated using the VESTA software; the cif file was obtained from The Cambridge Crystallographic Data Centre.²⁶



Figure 6. Simulated XRD spectrum of Mg-MOF-74 powder.

An XRD spectrum obtained experimentally for Mg-MOF-74 particles synthesized is shown in Figure 7. Comparison of this spectrum with the simulated one in Figure 6 allows for further characterization of the MOF obtained.



Figure 7. XRD spectrum of experimentally-synthesized Mg-MOF-74 powder.

It is clear at first glance that the literature spectrum matches well with the experimentally obtained one. The most noteworthy peaks for comparison occur when 2θ equals approximately 7° and 12°. Not only do these peaks appear at the anticipated time on the experimental spectrum, but it is significant that the very first peak is significantly larger than the second. The simulated spectrum does show a higher intensity than the experimental, but the general trend remains. Furthermore, the two spectra align in the presence of other, smaller peaks that occur at later angles on the spectra: roughly 14°, 15°, 18°, 19°, 21°, 22°, and so on. These peaks can be

observed on both the simulated and experimental spectra, though they are broader on the experimental one.

A second XRD spectrum, obtained with Mg-MOF-74 particles synthesized on a different day, is shown in the Appendix, for further comparison. The spectra, though not fully identical, are very similar, with the noteworthy peaks matching up. This reproducibility verifies the accuracy of the synthesis process, confirming that the materials synthesized were consistently successful MOFs, specifically successful Mg-MOF-74's.

Mg-MOF-74 films were synthesized in a vapor-assisted conversion process, similarly to the particle synthesis process. The silicon wafers were washed via sonication for 10 minutes with 10 mL each of deionized water, acetone, and isopropyl alcohol. In later experiments, graphene oxide was synthesized onto the wafers in an additional layer. This was done to prevent the MOF from filling in the porous channels of the substrate—this is less relevant when the silicon wafer substrate is used, but very relevant when a permeable substrate such as anodized aluminum oxide is used.¹ Hence, the graphene oxide layer is synthesized for completion of the experiment.

First, 40 mg (0.2 mmol) of H₄DOT were combined with 5.5 mL of DMF, 5.5 mL of ethanol, and 57.2 μ L (1 mmol) of HOAC. Separately, 461.538 mg (1.8 mmol) of Mg(NO₃)₂• **6H**₂O was combined with 3.6 mL of deionized water. The Mg(NO₃)₂ solution was slowly added to the H₄DOT solution. Then, 1.9 mL of 0.76316 M NaOH was added dropwise to the solution, while stirring and watching for precipitate formation. The solution should not be cloudy; the solution was thus sonicated until it was fully clear with no precipitate. A dilution solution was mixed from a 1:1:1 mixture of DMF:ethanol:H₂O. 2.5 mL of the precursor solution was diluted with 4 mL of this dilution solution. A vapor source was mixed from a 12:1:1 mixture of DMF:ethanol:H₂O. 4 mL of vapor source was added to each autoclave; 50 μ L of the diluted

precursor solution was placed on a silicon wafer in the autoclave. The solutions were heated at 100°C for 24 hours. The subsequently obtained films were washed via soaking with DMF three times and anhydrous methanol three times. The washing liquids were switched out every day over the course of six days. A photo of a set of MOF films taken during the washing process can be found in the Appendix. This process was repeated multiple times to gain experience with the synthesis process, as not every synthesis attempt resulted in usable films, particularly at first, and to investigate the different aspects of the synthesis. During one trial, an attempt was made to use 100 μ L of the precursor solution; however, this resulted in incorrectly adhered films that were too wet even after drying. The films obtained ranged in color from yellow, to green, to purple—almost iridescent. The majority of the films synthesized appeared yellow due to a layer of MOF particle powder that formed atop the film; once removed using scotch tape, the film appeared yellow and purple in different places. Many of the films additionally synthesized with a hole in the very center, where the concentration of precursor solution was greatest given the nature of a drop's shape. This was partially solved as 50 μ L of precursor solution was used rather than 100 µL, but still formed occasionally. A photo of two dried, finished films is shown in the Appendix.

Scanning electron microscopy (SEM) was further used to characterize the MOF films. A JEOL SM-31160 instrument was used to obtain the images. SEM involves scanning the surface of a material with a beam of electrons, which interact in different ways with the atoms in the material to produce varying signals, which are translated into an image of the sample surface. Figure 8 below shows SEM images experimentally obtained for the Mg-MOF-74 film synthesized.

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Figure 8. SEM images of experimentally-synthesized Mg-MOF-74 film.

These images clearly illustrate the presence of a film, given the lack of the normally-smooth silicon wafer surface. Though a basic conclusion, this shows that the film growth was successful. Given how closely zoomed in these images are, it is difficult to tell if the pattern of the growth is uniform or not; however, despite the presence of some larger clusters and particles, there is indication that the film does have a regular pattern. Figure 8(b), for example, shows a fairly consistent pattern of growth—this is important due to the aforementioned structure of the MOF. SEM images of Mg-MOF-74 films synthesized in a similar procedure, by a different group, for a different project, are shown below in Figure 9 for comparison purposes.



Figure 9. SEM images of Mg-MOF-74 film. Scale bar is 2 μm. Reprinted with permission from Ref.²⁷ Copyright 2021 American Chemical Society.

Though at first glance these images seem vastly different from those in Figure 8, this is largely due to the difference in scales used. The images in Figure 9 are much further zoomed out than those in Figure 8, hence one is able to see the uniformity of the growth at a distance better. Considering the closer scale of the images in Figure 8, it is reasonable to identify the particles as the ones seen from a further distance in the images in Figure 9. While these images cannot confidently be used to characterize the synthesized MOF further, they eliminate the possibility of error; we know that the SEM images should not look in any way drastically different from the way they appear. The film growth appears as clusters with no discernible pattern or shape, from the SEM image at least, as is the case with the experimentally-obtained ones as well.

Additionally, it is worth noting that each synthesis was repeated multiple times in order to gain repeated exposure to the procedure, achieve adequate experience in successful syntheses, and ensure reproducible results of the powder and films.

One major issue with the synthesis process that was encountered was in the addition of the NaOH during the film synthesis process. As noted, the NaOH had to be added dropwise with vigorous stirring to avoid precipitate formation, and even so it did occur. To fully avoid the buildup of precipitate during this addition, the addition of the NaOH had to be slowed down, to about one drop every 4-5 seconds. Given that the synthesis called for 1.9 mL of NaOH, this translated to practical issues, as one needed to manually pipet one drop, wait about 5 seconds for it to dissolve fully, pipet another singular drop, etc. This portion of the procedure was prone to error: if drops were pipetted in succession too quickly, the solution would precipitate and hinder film growth, down the line. As such, an interest was developed in optimizing this process. To accomplish this, the use of a syringe pump was investigated. For this, a Harvard Apparatus PhD Ultra instrument, with a thin tube connected, was loaded with the NaOH solution, which was primed to reach the end of the tube, and positioned to pump into the reaction flask, set upon a magnetic stirring plate. A photo of the syringe pump set-up is shown in the Appendix. The instrument was programmed to initially drip at a rate of 0.2 mL/min for the first drop or so, at which point the rate was decreased to 65 µL/min. Repeated syntheses using the syringe pump apparatus revealed that the set-up yielded precipitate-free precursor solutions, and films that were of comparable quality to those previously obtained via the manual pipetting. Furthermore, the syringe pump ensured more consistent outputs between trials, eliminating user error from the pipet slipping and ensuring precipitate-free solutions every time.

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IX. Conclusions and Next Steps

This project set out to investigate the synthesis of Mg-MOF-74, in the context of the larger magnesium battery project—one piece of the larger puzzle. We have demonstrated successful, repetitive synthesis of the MOF in question, showing a viable, replicable procedure with the appropriate characteristics to be successful in a battery context. Characterizations of both the MOF particles and film have shown not only the correct identification of Mg-MOF-74, successful film growth, and a semi-uniform film pore surface. These are encouraging markers for further work with Mg-MOF-74 and this synthesis procedure. Furthermore, this work has enabled the development of a rechargeable magnesium battery to proceed one step further, as the complete development of the MOF separator is vital to the success of a Mg-Br battery. The importance of this battery, and thus this work, has already been discussed, but should not be overlooked. Furthermore, the development of the syringe pump mechanism additionally enhances the synthesis procedure, as it streamlines the process and makes the quality of precursor solutions, and thus films, more consistent and successful. This is another important development in the context of this research project.

To further investigate Mg-MOF-74 in the context of this project, there are a number of steps that need to be taken. Firstly, the films must be synthesized on a porous substrate, such as anodized aluminum oxide (AAO). The porosity of the AAO will allow for Mg²⁺ ions to pass through the substrate itself, through the MOF, in a manner that the silicon wafer does not allow for. This will enable true tests of the ability of the Mg-MOF-74 film to transport ions, allowing for further characterizations of the films and a test of their ion transport abilities. This is a vital next step, as the MOF film must be able to transport ions in the battery in order for the circuit to be complete.

To that end, in order to test this transport ability, the film needs to be placed into a test battery as a separation layer between different electrolytes. The charging and discharging cycles of the Mg-Br battery will be observed, with the Mg-MOF-74 film acting as a selective ion transport mechanism. This should be done with films grown on AAO substrate, with a graphene oxide layer buffer, to ensure the appropriate ions pass through both the MOF and the substrate properly. The battery tests will hence allow one to evaluate the effectiveness of the MOF in its appropriate context, and evaluate further issues.

Furthermore, beyond the scope of this research project, it may be worthwhile to test Mg-MOF-74 as a separatory material in a variety of magnesium batteries, rather than only Mg-Br. This will allow for a broader understanding of the mechanisms of different magnesium batteries.

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XII. Appendix



Figure 1. Second XRD spectrum of experimentally-synthesized Mg-MOF-74 powder.



Figure 2. Photo of the synthesized MOF particles.



Figure 3. Photo taken of the MOF films during the washing process.



Figure 4. Photo of the synthesized MOF films.



Figure 5. Photo taken of the syringe pump setup