Synthesis, Characterization and Application of Mayenite

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SYNTHESIS, CHARACTERIZATION AND APPLICATION OF MAYENITE

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Materials Science and Engineering

by
Vincent Nicholas Phaneuf
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Accepted by:
Dr. Jianhua Tong, Committee Chair
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Dr. Kyle Brinkman
ABSTRACT

The mineral mayenite (12CaO•7Al2O3, C12A7), possesses a unique cage structure which allows the entrapment of anions due to the positive charge of the cage. The most abundant form of this mineral is C12A7:O\textsuperscript{2-} which exhibits high oxygen conductivity. However, the oxygen can be removed from the cage by reduction and other anions such as OH\textsuperscript{-}, H\textsuperscript{+}, Cl\textsuperscript{-}, and even e\textsuperscript{-} can be substituted in the cage. When electrons act as the anion in the cage, the material is classified as an electride. Mayenite electride shows promising properties such as metallic-like conduction and is a room temperature stable inorganic electride. The cages don’t necessarily need to be occupied by just one anion. It is possible to have a mixture of anions of different species in the cages of mayenite. Through mixed anions present in the cages, mixed conductivity becomes possible. With H\textsuperscript{+} ions and electrons inhabiting the cages of mayenite, it is theoretically possible to have hydrogen permeate through the cages. This allows the material mayenite to be used as a hydrogen permeable membrane. Other applications of mayenite include catalysts for ammonia formation, as well as an energy material for the cathode and electrolyte of a solid oxide fuel cell. To have a hydrogen permeable membrane, the membrane should be fully dense with as many charge carriers as possible to manifest high permeability without allowing molecules to diffuse or permeate through the membrane. This work focuses on the synthesis of mayenite with mixed conductivity to act as a hydrogen permeable membrane. Different dopants were tested such as doping a thin membrane with iron to allow the membrane to be fully dense. Silicon was also investigated as a dopant to replace aluminum sites as to create cages with higher positive charges with a goal of creating a doped mayenite with higher electron densities. Characterization was completed to show that the structure remained when doping, and that doping with silicon did indeed increase the electron density. Work was done to investigate the permeability of hydrogen through a thin membrane of mayenite.
DEDICATION

I dedicate this work to my caring & supporting parents Valerie & Jean Phaneuf
as well as my loving fiancée Lucy Mayers.
ACKNOWLEDGEMENTS

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CHAPTER ONE

INTRODUCTION

1.1 Motivation & Goals

As we progress into our future, there must be a drive towards sustainability. The use of fossil fuels adds large amounts of emissions to the environment, which causes ecosystem changes. These changes can disrupt the natural cycles we depend upon to provide us stable climates, clean water to drink, and healthy food to eat, making our society unsustainable. Therefore, we have to devote ourselves to leaning off our dependency on fossil fuels. Developing energy conversion and storage technologies such as fuel cells, solar cells, batteries and membrane reactors can use renewable energy sources such as sunlight, wind and biomass. Specifically, hydrogen which can come from water electrolysis using renewable electricity, plays a crucial role in developing new energy technologies. The materials used in hydrogen production, purification, and storage are critical for successful energy technologies. The chosen energy materials should have the properties to satisfy the high efficiency and the characteristics to be sustainably sourced and economically viable.

This work focuses on discovering new earth-abundant and high-performance energy materials for hydrogen-permeable membranes. As a potential hydrogen-permeable membrane candidate, the material must have high hydrogen permeance and complete hydrogen selectivity. Here, we select the mineral mayenite (12CaO•7Al₂O₃, C12A7) as a potential candidate to be used as a hydrogen-permeable membrane. The goals of this
research include: i) synthesis of dense, highly conductive mayenite, ii) demonstration of
the transport of hydrogen with permeation tests performed, and electrochemical
characterization of charged species transport properties for explaining hydrogen
permeation.

The current chapter introduces mayenite materials giving the background
information needed to understand how it possesses the properties required for energy
conversion and storage device applications. Synthesis of mayenite compounds
accommodating the varying forms of ions that can transport in mayenite structure are to be
summarized. Properties that resulted from the variable caged anion species are to be
introduced. Applications of mayenite are to be discussed and linked to the required
properties. Lastly in this chapter, mayenite’s conductivity is to be examined concerning the
type of mayenite and the environment in which the conductivity took place. Through the
conductivity & atmospheric relation, possible energy devices can be proposed and tested.

1.2 Mayenite Basics - Crystal Structure, Properties & Applications

Mayenite is a material of interest due to its earth-abundant raw components,
calcium and aluminum oxides, and the ability to accommodate versatile anions, including
electrons in its caged structure. Aluminum is the third most abundant resource, and calcium
is the 5th most abundant resource in the crust [1]. Due to the elements’ natural abundance,
the raw materials for mayenite are inexpensive even though they may require processing
to reach the desired form from their natural mineral. Creating a useful product from a
naturally abundant material is highly valued and is more sustainable than hunting rare earth elements for novel applications.

Figure 1.1 shows that mayenite has an antizeolite cage-like crystal structure. A zeolite structure has a framework usually composed of aluminum and silicon surrounding cavities occupied by cations, while antizeolite is just a zeolite structure that hosts anions instead of cations. The mayenite unit cell consists of a positively charged framework ([Ca$_{24}$Al$_{28}$O$_{64}$]$^{4+}$) comprising 12 cages (Figure 1.1a). The size of a single unit cell is around 11.98 Å [3], and the diameter of a single cage is ~0.4 nm [4]. Figure 1.1 b and c schematically shows the single cages composed of Ca, Al, and O. The openings to the cage are approximately 0.1 nm in diameter and cause this material to be nanoporous. The opening size is the limit as to what anion the cage can accommodate. In the Ca$_{24}$Al$_{28}$O$_{64}$ (C12A7:O$_{2}^-$) unit cell structure, two oxygen ions occupy two of the twelve cages. These two oxygen ions are responsible for the high oxygen ion conductivity found with C12A7:O$_{2}^-$ [5]. The anions such as hydrogen, hydroxide, chloride, fluoride, sulfur ions or even electrons can replace O$_{2}^-$ ions to occupy the C12A6 cages. The occupancy of free electrons in the C12A7 cages form mayenite electride (C12A7:e$^-$) and has recently attracted significant attention because it is a room temperature stable inorganic electride. Compared to C12A7:O$_{2}^-$, the electride can theoretically have double the amount of anions per unit cell due to the charge difference of O$_{2}^-$ and e$^-$. 
Figure 1.1 a) The unit cell of mayenite (12CaO•7Al2O3) b) The individual cage structure of mayenite c) An example of a negative ion, in this case O^{2-}, occupying the space in the cage [2]

The free oxygen ions in the oxygen mayenite cage (C12A7:O^{2-}) allow oxygen ion migration to ensure mayenite’s oxygen ion conductivity [5]. However, mayenite’s ionic conductivity is less than yttria-stabilized zirconia (YSZ) by a factor of 8-10 in the temperature range of 280-1350°C. Although it is a significant deficiency, C12A7 contains no rare earth elements and is a much less expensive alternative to YSZ. Overall, C12A7:O^{2-} is an electronic insulator. Therefore, the mayenite oxide usually is a potential candidate in applications such as solid oxide fuel cells, oxygen sensors, super-capacitors, oxygen pumps and even batteries.

It is crucial to bear in mind that the mayenite synthesis conditions decide what anions end up in the cages. In a study, Hosono et al. [7] found that synthesis in wet and dry
air at different temperatures had different results in what type of oxygen species occupy the cages (O$^{2-}$, O$, \text{OH}^-$). The different types of oxygen species resulted in different ionic conductivities across the material. Also, the different types of oxygen species allowed different applications. For example, the hydroxide ion involved with hydrogen species can potentially find applications for reactions that would require hydrogen.

Mayenite electride (C12A7:e$^-$), formed when electrons replaced free oxygen ions to occupy the mayenite cages. Kim et al. [8] showed that mayenite samples underwent an insulator to metal transition when the electron density reached above $10^{21}$ cm$^{-3}$ in the mayenite structure. This vital discovery not only demonstrated the high metallic-like conductivity of a stable inorganic electride but also set a goal of achieving an electron density greater than $10^{21}$ cm$^{-3}$. The conductivity of the mayenite electride further increased with increasing temperature. There is a limit to increasing the temperature to achieve higher conductivity as at temperatures above 1400°C the material thermally decomposes and melts. Another essential property of this electride material is its ability to donate the electrons found within its cages [10]. Mayenite electride possesses a low work function of 2.4 eV as was found by Toda et al. [11]. The low work function of the electride allows it to easily donate electrons as the work function is the minimum amount of energy required to remove an electron from the material. Being stable at room temperature and elevated temperatures is an additional property that attracts attention to this material as this property allows for easier handling and storage creating the opportunity for viable applications.
Mayenite materials have found a wide range of applications. Specifically, for mayenite electride we can see many applications in Figure 1.2. Mayenite electride can act as a cathode material in fluorescent lamps, as an electron-injection layer in organic light-emitting diodes and plasma display panels, as a chemical reductant, as parts wires, as electrodes. More importantly mayenite electride served as an excellent catalyst component for several catalytic reactions. Catalyst applications of mayenite electride include the
production and decomposition of ammonia, the reforming of bio-oil, splitting carbon
dioxide, and as an electrocatalyst for fuel cells.

Mayenite electride has many different potential applications, but one application
of more considerable interest out of the previously mentioned applications is ammonia
synthesis. Traditionally, ammonia synthesis catalysts encountered the \( \text{H}_2 \) poisoning effect,
diminishing the catalytic activity under high hydrogen concentration. Kammert et al. [12]
showed that mayenite electride supports resolved the hydrogen poisoning problem for Ru
catalysts compared to other metal oxide catalyst supports. \textbf{Figure 1.3 a} indicated Ru
mayenite electride catalysts outperforms ruthenium catalysts based on other well-known
supports. The electride compared to the oxide shows a drastic increase in the turnover
frequency as well. It suggests that this performance increase for the electride based catalyst
compared to the oxide-based catalyst is due to the electride’s ability to donate electrons to
ruthenium. \textbf{Figure 1-3 b} shows the mayenite electride’s ability to withstand hydrogen.
Rather than decreasing, resulting from \( \text{H}_2 \) poisoning, mayenite electride increased turnover
frequency when more hydrogen is present. It suggests this lack of hydrogen poisoning on
mayenite electride is due to an increase of reactive intermediates that form on the surface
of ruthenium which could be created by mayenite electride donating electrons to the
ruthenium. Overall, the ammonia synthesis catalyst is one of the most exciting applications
of mayenite electride.
1.3 Synthesis of Mayenite Materials

The synthesis of mayenite materials can vary greatly depending on the desired anion, size, and shape of the final products. In addition to pursuing the desired anions in the mayenite structure, the mayenite synthesis is also concerned with achieving high-surface-area powders, defect-free thin films, single crystals, and dense/porous membranes. Depending on the application, the selected methods must fit the required properties such as a high surface area for catalyst support or a fully dense thin film for fuel cell electrolyte membrane. This section reviews various methods for synthesizing mayenite electride powders because of the extensive use as ammonia synthesis catalyst support and potential start materials of hydrogen-permeable membranes.
In the earlier work, Matsuishi et al. [13] developed a seven-step method to prepare mayenite electride powders. The method involved the synthesis of a mixture of C12A7 and CaO•Al₂O₃ (CA) from α-Al₂O₃ at 1300°C in ambient air, elimination of excess oxygen species and hydroxyl groups incorporated in the cages of C12A7 by heating at 1100°C in a dynamically evacuated silica tube, and formation of C12A7 electride from C12A7+CA+Ca in evacuated silica tube at 700°C. This method synthesized C12A7 electride powders with high electron densities of 2.3×10²¹ cm⁻³, near the theoretical maximum of 2.33×10²¹ cm⁻³. However, this seven-step process is very lengthy and involves the use of many sealed and evaluated environments. Additionally, this method requires a glove box filled with argon to handle the calcium powder, adding more difficulties.

Inoue et al. [14] focused on mayenite electride as catalyst support for ammonia synthesis and developed a synthesis method that produced powders with a high surface area. Their method involved a hydrothermal reaction of precursor calcium and aluminum hydroxides, a following cage evacuation in a vacuum, and a final reduction with CaH₂. The resulting electride from this method showed a very high surface area, which was excellent for catalysis. However, the C12A7 electride synthesized from this method yielded low electron densities ranging from 0.7-1.6×10²¹ cm⁻³. The hydroxide and oxide ions in the primary C12A7 powders synthesized by the hydrothermal process were difficult to thoroughly remove from the cages, so that the evacuation and reduction of the cages
resulted in not all the cages filling with electrons. CaH₂ is a dangerous material to deal with due to the reaction of CaH₂ with water.

A single crystal of mayenite electride could be attractive as a hydrogen-permeable membrane as there wouldn’t have to be conduction over any grain boundaries, increasing the overall conductivity and thus increasing the permeation flux. Matsuishi et al. [15] synthesized a single crystal of mayenite electride with a high electron density of $2 \times 10^{21}$ cm⁻³. This method involved growing C12A7 crystals using a floating zone method and then treating the single crystal with metal calcium shots in a heated and vacuumed silica glass tube for up to 240 hours at 700°C. Unfortunately, a CaO impure layer formed on the crystal surface. Moreover, the treatment for 240 hours is quite a long time and is a significant disadvantage of this method. The utilization of a single crystal may also be challenging to apply in a hydrogen permeation testing apparatus.

A C12A7 pellet may be more appropriate for performing a hydrogen permeation. Zou et al. [16] developed a method for the direct fabrication of mayenite electride pellets. Their method involved a solid-state reaction of CaCO₃ and Al₂O₃ at 1250°C for 8 hours. The resulting powders would then be ground, mixed, and pressed into a pellet followed by a reduction in a carbon crucible in an inert atmosphere of N₂ at temperatures ranging from 1250 °C to 1500 °C. Referring to Figure 1.4 a & b, it can be seen that this method fabricated a fully dense pellet. Therefore, this method could fabricate a C12A7 electride pellet with the desired microstructure to serve as a hydrogen permeation membrane. This
method can also be completed efficiently without requiring specialized equipment and complicated handling atmospheres, and the involvement of dangerous precursors. However, the resulting electron density was low. The electron density from this method ranges depending on the reduction temperature. Higher reduction temperatures yield higher electron densities. A reduction at 1250°C yields an electron concentration of $4.9 \times 10^{19}$ e$^-$/cm$^3$, while a reduction at 1450 °C yields an electron concentration of $2.3 \times 10^{20}$ e$^-$/cm$^3$, which is more than one order of magnitude lower than the maximum theoretical electron density.

**Figure 1.4** a) Photograph of a pellet synthesized at 1450 °C b) SEM cross-section view of the same pellet [16]

### 1.4 Electrical Conductivities of Mayenite Materials

It has been well known since 1988 that mayenite is a competitive oxygen ion conductor, as discovered by Lacerda et al. [5]. **Figure 1.5** provides the oxygen ion conductivity of C12A7 oxide versus operating temperature from 300-1450°C, slightly
lower than the conventional yttria-stabilized zirconia. A study conducted by Eufinger et al. [17] showed that substituting oxygen ions in the C12A7 cages with different anions such as nitrogen, sulfur, fluorine, chlorine and even cyanide allowed conductivity based on the corresponding anion in the mayenite structure. Compared to $\text{O}^{2-}$ ions, the substituted anions usually had higher activation energies for the ion conduction through the material. Therefore, the anion substitution for oxygen ion usually resulted in lower conductivities in comparison with oxymayenite. In the presence of an oxygen-containing atmosphere, the anion substituted mayenite samples would become oxidized, reverting to oxymaynate.

In addition to accommodating different anions, the C12A7 mayenite cages allow the presence of free electrons to form mayenite electride, an excellent electronic conductor. Hosono et al. [18] found that mayenite electride has an electronic conductivity as high as 1500 S/cm. This high conductivity is due to the transport of electrons through the cages of mayenite. This high conductivity can also be associated with the high electron density of $\sim 1.9 \times 10^{21}$ $\text{e}^-/\text{cm}^3$. 
Furthermore, the presence of certain gases (e.g., hydrogen) caused significant changes in the conductivity of mayenite electride and oxymayenite materials. Dong et al. [19] found that mayenite could act as a mixed ionic and electronic conductor because of the coexistence of differently charged species (e.g., electron, hydrogen anion, oxygen ion, and proton). Dong started with a pellet of C12A7:O$^\text{2-}$ oxymayenite, then reduced this pellet in 75% H$_2$ 25% N$_2$ atmosphere to introduce hydrogen anions in the C12A7 cage. The exposure to UV radiation partially replaced the hydrogen anions with electrons. This series treatment allowed the formation of O$^\text{2-}$ ions, H$^-$ ions and electrons in the mayenite structure, probably resulting in mixed proton/hydrogen anion, electron and oxygen ion conductivity. The mixed conducting electrical properties qualify C12A6 mayenite materials with many novel energy technology applications (e.g., hydrogen separation membranes, fuel cell
electrodes, and gas sensors) The mixed ionic and electronic conductivity allows C12A7 mayenite to serve as electrode or electrode scaffold for solid oxide fuel cells [35]. The mixed proton/hydrogen anion and electron conductivity allows C12A7 mayenite to serve as a hydrogen-permeable membrane as described in Figure 1.6. The difference in hydrogen concentration illustrated by the slanted line through the membrane can serve as the driving force. The mixed proton/hydrogen anion and electron allow the hydrogen permeation without external electrical circuit and powered input.

![Figure 1.6](image)

**Figure 1.6** Mixed proton-electron conduction membrane demonstrating a hydrogen permeable membrane [20]

### 1.5 Objectives and Approaches

Since mayenite has shown mixed proton/hydrogen anion and electron conductivity, it should act as a hydrogen permeable membrane theoretically. However, it has not yet been shown that this material can be used as a hydrogen-permeable membrane. The overarching goal of this work is working towards the application of mayenite electride as a hydrogen-permeable membrane. This thesis objective is to experimentally investigate the
mayenite material’s feasibility of serving as a hydrogen-permeable membrane by testing a fully dense mayenite membrane with desired mixed conductivity. This dense membrane should be thin enough to allow fast hydrogen permeation through the membrane for achieving measurably high hydrogen permeation flux. However, a thin membrane may need support to be mechanically strong enough to resist cracking from the stresses induced during performance testing. This thin membrane should also have a high concentration of electrons and hydrogen to ensure high hydrogen permeability intrinsically. Initially, in this work, the mayenite oxide and electride powders must first be synthesized. Then the thin and dense membrane will be fabricated, and the hydrogen permeation performance will be tested. Work will be completed to investigate various methods to synthesize the powder. Dopants will be investigated to increase the electron density in the membrane. Different methods will be tried to fabricate the dense and thin membranes, including adding sintering additives to achieve a fully dense membrane. Lastly, a method for testing the permeability of hydrogen through the dense membranes will be performed.
CHAPTER TWO

SYNTHESIS AND CHARACTERIZATION OF MAYENITE POWDER

The prerequisite for any mayenite applications, including hydrogen-permeable membrane, is to synthesize mayenite powders with the desired properties. It is crucial to develop a facile and time-efficient synthesis method by using readily available equipment to produce pure mayenite powders with a high electron density from cost-effective and nonhazardous precursors. Moreover, the synthesized mayenite powder should also be easy to form green ceramic parts (e.g., thin films and planar pellets). The desired properties of the as-synthesized mayenite powders are to be achieved for ensuring high-performance mayenite-based devices (e.g., hydrogen-permeable membranes).

The goal of this chapter is to describe the methods we developed for synthesizing mayenite powders. It identifies aspects that were not successful and investigates the resulting powders from each method. A doped version of mayenite is to be introduced to increase the maximum electron density of the resulting electride powders. The applicability of these powders for a hydrogen-permeable membrane is to be discussed.

2.1 Aluminothermic Solid State Reaction

We developed a facile and cost-effective aluminothermic method to synthesize mayenite electride powders with high electron densities on a much larger scale than most of the methods reported in the literature [21]. This method involves combining calcium oxide (CaO), gamma phase aluminum oxide ($\gamma$-Al$_2$O$_3$) and aluminum powders obtained
from Sigma-Aldrich. The combination follows a stoichiometric amount with a ratio of 12:6.9:1.4 CaO:γ-Al₂O₃:Al. This ratio follows a 10% addition of aluminum metal powders based on the total aluminum amount. The powders would be combined, and ball milled for 6 hours using 3mm YSZ without any solvent. It is essential to not ball mill the mixture for too long as the powders start to aggregate inside the ball milling container. If aggregation occurs, one cannot be sure that the powders form a homogeneous mixture. After ball milling, the powders would then be placed in an alumina crucible with an alumina lid & calcined at 1250 °C for 12 hours under flowing argon atmosphere in a tubular furnace. A temperature ramp and decline rate of 5°C/min were used to increase and decrease the temperature to 1250°C. The argon flow through the chamber would be set to 100 ml/minute. A basic schematic can be seen in Figure 2.1. A solid-state reaction occurred that utilized the aluminum metal powders as a reducing agent. Between Dong’s work and the method used in this work, it was found that increasing the calcination time from 8 hours to 12 hours caused a more consistent result with higher electron densities. In this work, a cylindrical crucible was used rather than a rectangular crucible. The effect of the cylindrical crucible will be discussed in the following sections.
One crucial aspect of this method is the environment inside the furnace during calcination. For the resulting mayenite to be of high electron concentrations, the environment must allow the reduction reaction. It means that there must be no oxygen or humidity present in the tubular reactor. It is easy to tell if oxygen was present in the reactor from the resulting electride powders’ color. Typically, the electride powders synthesized from this method should be completely black as seen in Figure 2.2, indicating the formation of electride with high electron density. Mayenite powders synthesized in the presence of oxygen or humidity led to C12A7:O2− or C12A7:OH−. The color of these two mayenite materials species is white. Therefore, any white color found in the resulting powders is due to water or oxygen being present in the furnace. The purging of the reactor with argon for 2 hours before calcination was needed to eliminate oxygen and humidity from the reactor. If the reactor was not well purged, the resulting powders would look
similar to those shown in Figure 2.3. Not purging the chamber beforehand led to oxymayenite also being formed. The formation of the grey and white powders in Figure 2.3 is due to the cylindrical crucible, as previously mentioned. The powder in the region closest to the lid, which in Figure 2.3 would be the left side of the powder block, would often be a mixture of white, grey, and black particles. The residual oxygen present in the reactor’s lid region caused the formation of oxymayenite rather than mayenite electride. The purging of the sealed reactor chamber with argon for a minimum of two hours was required to prevent the formation of any mayenite oxides. A flowmeter was further used to measure the inlet and outlet argon fluxes to and from the reactor chamber for ensuring no leakage of atmospheric oxygen to the reactor. If the reactor is gas-tight, there should be almost no difference between the inlet and outlet.

Figure 2.2 A batch of ground electride powders resulting from the aluminothermic method
If one were to use this method to prepare mayenite powders suitable for fabricating hydrogen-permeable membranes (e.g., dense pellets of thin films), a mixture of argon and hydrogen gas could work as a protective atmosphere, which directly introduced hydrogen into the cages of mayenite and ruled out the residual oxygen more efficiently. During the reaction, hydrogen resulted in a mixture of white and black particles as seen in Figure 2.4. According to our previous work [21], a sample of mayenite containing hydrogen species (mayenite hydride) became green with exposure to ultraviolet radiation, proving hydrogen species’ existence in the mayenite structure. Our sample was bombarded with ultraviolet radiation utilizing a UV lame to check if the hydrogen species exist in the mayenite structure. It can be seen from Figure 2.5 that much of the sample has turned green, which proved the formation of mayenite hydride and electride while using a hydrogen and argon mixture as a protective atmosphere. With hydrogen and electrons present in the cages of
the mayenite, it should be possible to permeate hydrogen through this material utilizing the driving force of a concentration gradient of hydrogen.

**Figure 2.4** Aluminothermic synthesis of mayenite resulting from a reaction in an environment of 5% H₂ 95% Ar
In many synthesis methods that yielded high electron densities, a vacuum was often used [22]. In theory, applying a vacuum to the system while calcining should speed up removing oxygen and humidity from the reactor. A vacuum pump was used to help the evacuation of residual oxygen and humidity during the aluminothermic reaction. Before heating, a vacuum would be applied to the reactor, and then the reactor would be filled with the desired reduction gas of either argon or argon mixed with hydrogen flowing at 200 ml/minute. The applied vacuum was at ~12 psi. This vacuum evacuation process was performed three times to reduce the amount of oxygen and humidity present in the reactor. Before applying the vacuum, a leak test was performed using the difference in the gas flow of the inlet and outlet of the reactor, which must be equal for the leak test to pass. Soap
water was also applied to joints in the reactor apparatus to test for potential leaks. If leaks were present, bubbles would appear in the areas where the soapy water was applied. After flushing the chamber three times, the desired gas would be re-introduced into the furnace at a flow of 20-50 ml/minute. The vacuum pump would still be left on and the applied vacuum would range from negative 1-2 psi. The heating temperature and time would remain unchanged at 1250 °C for 12 hours.

However, consistently applying a vacuum leads to a failed synthesis of mayenite electride. Figure 2.6 provides the photo of the resulting mayenite powder from continuously applying a vacuum to the aluminothermic reaction. The resulted mayenite powders are entirely white, indicating no formation of electride. The reason for the failed synthesis of mayenite electride turned out to be the reactor’s poor sealing, which was not gas-tight enough to hold the desired vacuum for the calcination time of 12 hours. The vacuum sucked oxygen into the reactor from the ambient atmosphere during the calcination process, which provided oxygen to the powders to form oxymayenite. The leak test using soapy water did not find leak locations of the reactor system. It was also worth noting that continued use of the alumina tubes in the furnace would warp the tube, and eventually small cracks in the alumina tube would appear. Thus, new alumina tubes were used to attempt to fix the leak. However, the reactor based on the new alumina tube also resulted in completely white powders. It was also thought that maybe the leak could be coming from an area before the gas delivery system to the furnace. To see if this was the issue, instead of gas flowing through the gas delivery system, a tank of argon was used to supply
gas directly to the reactor. Supplying gas directly from the gas cylinder also failed to produce mayenite electride. Thus, we concluded that the system used for this synthesis was not gas-tight enough to have a vacuum without pulling gas in from the surrounding environment. Therefore, the application of continuous vacuuming to the aluminothermic process did not turn out to be an effective way for synthesizing mayenite electride powder.

Figure 2.6 Mayenite powders resulting from applying a vacuum to the aluminothermic method

This aluminothermic method yielded large amounts of mayenite electride in a single-step synthesis. These powders can then be processed into a thin membrane for permeation testing. However, it was not easy to press these powders into a pellet, without proper binders. The binders used in this work were pure water as well as a 5% PVA aqueous solution. Both binders were detrimental to the electron concentration as water in the pellet
caused OH$^-$ ions to be introduced into the cages, lowering the final electron density. The presence of water could also cause a reaction to occur that formed an impurity of Ca$_3$Al$_2$(OH)$_{12}$. In our previous work, Dong et al. [23] proved that C12A7:e$^-$ did indeed react with water to form two other phases of Ca$_3$Al$_2$(OH)$_{12}$ and Al(OH)$_3$. The PVA presence was also an issue because the PVA burned during sintering, leaving behind voids in the membrane. These voids finally resulted in the low relative density of the membrane and might cause poor hydrogen selectivity. Thus, other synthesis methods must also be considered to fabricate a thin dense membrane for hydrogen permeation.

### 2.2 Sol-Gel Synthesis

It is essential to fabricate fully dense electride pellets for hydrogen permeation. The high-quality mayenite powders allowing the fabrication of a fully dense mayenite electride membrane is still necessary. The sol-gel method also developed in our previous work [23] may serve well for this purpose. This sol-gel method involved forming a clear solution, viscous sol/gel, which turned into a charcoal by proper drying. The resulting primary powders would be ground, calcined, and lastly reduced to form mayenite electride powder. This method could prepare high-quality powder, allowing for the fabrication of fully dense electride pellets.

These chemicals purchased from Alfa-Aesar were used directly without further purification. The stoichiometric amount of calcium nitrate tetrahydrate (Ca(NO$_3$)$_2$·4H$_2$O) and aluminum nitrate nonahydrate (Al(NO$_3$)$_3$·9H$_2$O) in a molar ratio of 12:14 dissolved in
400 ml of deionized water in a beaker to form a clear solution. Ethylene diamine tetraacetic (EDTA) acid and citric acid monohydrate (C₆H₈O₇·H₂O) with ratios of 1 and 1.5 to the total metal ions respectively were added to the solution for chelating the metal ion. Ammonium hydroxide was added to the solution to adjust the pH value to around 10. Usually, eight additional pipettes were added to the solution to ensure an excess of ammonium hydroxide. The solution was heated on a hot plate at 250°C for about 6 hours to vaporize excess water to turn the solution into viscous sol/gel. The viscous sol/gel was transferred to a box oven where it was heated at 150°C for 48 hours. At this point the sol/gel changed into black charcoal. This charcoal was ground utilizing a mortar and pestle and was then calcined.

Depending on the calcination temperature, there were two useful outcomes. If the charcoal was calcined at 1200°C for 10 hours, the C12A7 oxymayenite phase formed. If the charcoal was calcined at 1000°C for 10 hours, two calcium aluminate phases of CaAl₂O₄ (CA) and Ca₃Al₂O₆ (C₃A) formed. The ramp rate for both outcomes is 5°C/minute. The further reduction in a graphite crucible could turn the C12A7 phase or the CA+C₃A powders into mayenite electride. The reduction temperature could range from 1200-1450°C for 6 hours. The ramp rate used to reduce powders was 5 °C/minute. To ensure that reduction took place, the environment in the furnace must be inert. Argon gas was used as the flowing gas. Like the aluminothermic method, before the reduction, it was also essential to sweep the furnace chamber for at least 2 hours to ensure all the oxygen or humidity has been evacuated completely.
If one were to use the sol-gel method to prepare dense pellets, pellets could be pressed from the powders after the calcination. The pellet was placed in a crucible surrounded by graphite powders for reduction. The lower temperature ramp rate must be used when sintering and reducing pellets due to the higher thermal stresses experienced with a high-temperature ramp rate. The reduction time must also be increased to 12 hours to ensure the pellet has completed the sintering process and become fully dense. Using either the mixture of CA & C3A or the pure C12A7 both resulted in mayenite electride after reducing in graphite powders.

2.3 Silicothermic Synthesis

One of the primary drives of this work was to synthesize mayenite electride powder with high electron densities. Therefore, a dopant with a higher oxidation state than aluminum was introduced into the mayenite framework to achieve a higher charge concentration. The undoped unit cell of mayenite can only have 4 out of the 12 cages occupied by electrons, decided by the +4 charge unit cell framework. If mayenite was doped with an atom with a higher charge and similar size than the host atom (i.e., Al) it might be possible to increase the number of cages that can be occupied by electrons. Silicon was chosen as the dopant of study due to the higher charge compared to aluminum atoms. Silicon was also an excellent candidate to substitute aluminum sites due to the small difference in ionic radii of aluminum and silicon.
The mayenite materials of $\text{12CaO}\cdot\text{5Al}_2\text{O}_3+\text{4SiO}_2$ (C12A5S4) and $\text{12CaO}\cdot\text{6Al}_2\text{O}_3+\text{2SiO}_2$ (C12A6S2) were chosen in this study. In the unit cell of C12A6S2, 2 $\text{Al}^{3+}$ sites were replaced with $\text{Si}^{4+}$. Therefore, the unit cell of C12A6S2 should have a charge of +6 instead of +4 and should be able to hold an additional 2 electrons per unit cell. In the unit cell of C12A5S4, 4 $\text{Al}^{3+}$ sites were replaced with $\text{Si}^{4+}$. Therefore, the unit cell of C12A5S4 should have a charge of +8 instead of +4 and should be able to hold an additional 4 electrons per unit cell. This would allow two-thirds of the cages in the unit cell to be occupied by electrons. The maximum theoretical electron density of C12A7 has been found by DFT and is $2.33\times10^{21}$ $\text{e}^-/\text{cm}^3$. For C12A6S2, theoretically there are 1.5 times the cages occupied by electrons. Therefore, the maximum theoretical electron density for C12A6S2 should be $\sim3.5\times10^{21}$ $\text{e}^-/\text{cm}^3$. For C12A5S4, theoretically two-thirds of the 12 cages would be occupied by electrons to satisfy the +8 charge of the unit cell. Therefore, the maximum electron density of C12A5S4 should be $\sim4.66\times10^{21}$ $\text{e}^-/\text{cm}^3$.

The synthesis of these silicon doped mayenite materials followed the same procedures as the aluminothermic method. CaO, $\gamma$-$\text{Al}_2\text{O}_3$, Al, and Si powders purchased from Alfa-Aesar were used for the synthesis without further purification. Compared to the previously mentioned aluminothermic synthesis, the CaO and Al metal relative ratios did not change. The Al metal was still 10mol% of the total Al+Si sites (14). Pure silicon powders with the ratios of 2 out of 14 and 4 out of 14 were added for synthesizing C12A5S4 and C12A6S2. The rest of the aluminum came from $\gamma$-$\text{Al}_2\text{O}_3$. Both pure Si and Al could work as reductant to help the direct formation of mayenite electride with high electron
concentration. The photo of the as-synthesized C12A5S4 mayenite electride powders is shown in Figure 2.7. The majority of the powder is black, while the white color is still observable. Visually, there was no difference between the resulting C12A5S4 and C12A6S2 powders. Therefore, the photo for C12A6S2 powder is not shown here.

![Figure 2.7 Resulting material from a silicothermic synthesis of C12A5S4](image)

2.4 Powder Characterization

2.4.1 Introduction

This section discusses the characterization techniques used to characterize the as synthesized mayenite powders by the method mentioned above. The main two techniques used were iodometry and X-ray diffraction (XRD). XRD was used to confirm that the resulting powder formed the mayenite phase, and to be able to identify impurities present
in the samples. Iodometry was a technique used to evaluate the electron density of the powders. The electron density is a critical property to decide the final mixed proton/hydrogen anion and electron conductivity. The desired high electron density in the membrane can result in high mixed conductivity and high hydrogen permeability.

The utilization of iodometry to determine anionic electron density in mayenite was first studied by Yoshizumi et al. [24]. They revealed that iodometry was a suitable method to evaluate the electron density by comparative studying using TGA, reflectance analysis, and electrical conductivity analysis. It was found that the iodometry results were in general agreement with the results obtained through the other methods. The basis of this iodometry technique lies in the following chemical equation:

\[
I_2 + 2e^- \rightarrow 2I^-
\]

The electrons trapped in the cages react with iodine to form an iodine ion. This method involves dissolving a small, known amount of mayenite electride powders in a \(1\times10^{-3}\) molar solution of \(I_2\). The moles of iodine should be in excess compared to the moles of electrons, so that the excess can be titrated, and the amount of iodine used can be calculated. Hydrochloric acid is added to the solution to allow the mayenite powders to dissolve fully. The ultrasonic bath can treat the solution to help the powder dissolve. The container holding this solution should be seal-able to prevent oxygen from reoxidizing the iodine. The container should also be opaque to light to prevent any reaction occurring with light. Once the powders are dissolved entirely, titration with sodium thiosulfate (\(Na_2S_2O_3\)) can start.
The solution can be transferred into a transparent container and the previous container can be washed with deionized water to ensure all the solution residues are transferred to the transparent container. A $1 \times 10^{-3}$ molar solution of sodium thiosulfate is used for the titration. The experimental setup for the titration is shown in Figure 2.8. In this set-up a burette is used to measure the amount of sodium thiosulfate added accurately. The starch solution is added to the solution to determine the endpoint of the titration better. Without the starch solution, it is more difficult to determine the endpoint of the titration. When all the excess iodine, which was not reduced by the electrons from the dissolved powders, completely reacted with the sodium thiosulfate, the titration reached the endpoint. At the endpoint, the solution's color changes from slightly violet to colorless (Figure 2.8). Based on the amount of sodium thiosulfate used, the amount of iodine not used in the reaction with electrons can be calculated. The amount of iodine that did react with the electrons can be found based on the total amount of iodine used and the amount of unreacted iodine. Using the amount of iodine that reacted with the electrons, the moles of electrons found in the sample can be calculated. Knowing the density of mayenite, the mass of mayenite used, and the number of electrons found in the sample, electrons per cm$^3$ can be calculated. Thus, the electron density is found. The equation is shown below:

$$\text{Electron density} = \frac{(\text{moles of electrons} \times 6.022 \times 10^{23})}{(\text{mass of C12A7 used/density of mayenite})}$$
Figure 2.8 Experimental set-up for the iodometry titration

X-ray diffraction (XRD) is the other primary technique used to characterize the powders synthesized in this work. Through XRD, it is possible to identify the as-synthesized powder’s crystal structure. It is also possible to determine if the sample is phase pure or if multiple phases are present. It can be completed by comparing the gathered spectrum resulting from a scan and comparing it to a phase database. It must be noted that XRD can only be completed for crystalline materials, as amorphous materials are unidentifiable through XRD. A Rigaku Ultima IV X-ray diffractometer was used in this work to complete x-ray diffraction measurements. Cu Kα was the radiation used in this diffractometer. Peak identification was performed using Jade software.
2.4.2 Characterization Results & Discussion

The first question that is often asked when synthesizing a material is, was it really synthesized? To answer this question, we can refer to the XRD data. The known elements presented in the as-synthesized materials allow using XRD to identify the materials' crystal structure. Initially, we studied the crystal structures for the mayenite powders synthesized using the sol-gel method and the aluminothermic method. Figure 2.9 provides the XRD results for these two samples. The powder synthesized by the aluminothermic method formed a phase pure mayenite electride. However, a krotite impure phase is present in the sol-gel method's powder besides the mayenite electride phase. The chemical formula for krotite is CaAl$_2$O$_4$ and is one of the two precursors (CA & C3A) to mayenite electride via the sol-gel method. Therefore, it's possible that in this specific sample, there was more CA than C3A, which caused the excess of CA to still be present after the reduction. In this specific sol-gel sample, reduction took place at 1250 °C for 6 hours. This impurity could also result from the CO$_2$ formed from graphite, and some residual oxygen in the system during reduction. In our previous work, Dong et al. [21] proved that the presence of CO$_2$ could inhibit the crystallization of mayenite, which would cause CA as an impurity. In the aluminothermic synthesis method, there was no carbon source for the formation of CO$_2$. Therefore, the CO$_2$ effect did not occur, allowing the formation of pure mayenite electride. From this comparison, we can conclude that powders from the aluminothermic method would be a better one for the fabrication of a hydrogen-permeable membrane due to the phase pure XRD result.
Figure 2.9 XRD results comparing the spectrums gathered from sol-gel precursors and from the aluminothermic method

XRD data was also collected for the silicon doped samples C12A6S2 and C12A5S4. The comparison between these two samples can be seen in Figure 2.10. It can directly be seen that neither samples formed a phase pure mayenite. The primary phase of both samples is C12A7, however both of them also had at least one impure phase, which can be indexed to margarite (CaAl₂(Al₂Si₂)O₁₀(OH)₂). This impurity is in the realm of possibility as all elements of this mineral are present in the silicon doped mayenite. Due to the high humidity of Clemson, it is possible that some small amount of water is available in the reaction to provide a source of hydroxides for margarite. C12A6S2 had one
additional impurity of CaAl$_2$O$_4$, known as krotite. Both samples were synthesized in the same conditions of 1250°C for 12 hours in an argon environment. Due to the presence of an impure phase containing silicon, it cannot be said that all silicon was substituted at aluminum sites in C12A7. However, it was observed that two samples had mayenite peaks that are slightly shifted to higher angles compared to the powder diffraction file for mayenite in the Jade software. This shift can be attributed to substitutions in the crystalline structure with an atom of a smaller radius. With a substitution of an element with a smaller radius, the crystal lattice experiences contraction, and the lattice parameter decreases. This causes a peak shift to higher angles. Silicon does indeed have an atomic radius smaller than that of aluminum. Therefore, it can be inferred that at least some silicon substituted into the aluminum sites of the C12A7 phase for C12A5S4 & C12A6S2. If one were to use either of these materials for a hydrogen-permeable membrane, the more phase pure sample would be preferred. However, one of the critical properties of an excellent hydrogen permeable membrane should be the high electron density. To better determine which dopant concentration would be better to use in a hydrogen-permeable membrane we should consider the iodometry results.
Figure 2.10 XRD results comparing the spectrums from the two silicon doped samples, C122A6S2 & C12A5S4

The iodometry results are shown in Table 2.1. The mayenite powder synthesized by the sol-gel method shows the lowest electron density. This electron density is relatively close to the one reported by Dong et al. in our previous work [23]. Compared to the mayenite electride powders synthesized from the sol-gel route, the mayenite electride powders synthesized through the aluminothermic route shows a much higher electron density. One possible explanation for the large difference in electron density between the mayenite electride powder synthesized from the sol-gel method and the mayenite electride powder synthesized from the aluminothermic method is that the aluminum metal in the
aluminothermic method is an excellent reducing agent for introducing electrons in the C12A7 cages. The carbon from the graphite crucible served as the reductant for turning the sol-gel precursor powder into mayenite electride power. The carbon reductant usually resulted in a mixture of CO and CO₂, a relatively ineffective reducing atmosphere for the formation of mayenite electride. It can also be noted that the electron density for the mayenite electride powder derived from C12A7:O²⁻ precursors is lower than that derived from CA & C3A precursors. This can be ascribed to the fact that the electrons are injected into the cages of mayenite while the cages are forming compared to the oxymayenite precursor where firstly, oxygen must be removed from the cages, then electrons can be injected. This extra step of removing the oxygen may slow the reduction down. Since both samples were reduced at the same temperature simultaneously, it would make sense that the route with the extra step that would take a longer time to reduce the entire sample, does indeed have a lower electron density.

Concerning the silicon doped samples, it is shown that doping with silicon did increase the electron density of the material. Also, as expected, it can be seen that the higher amount of silicon did synthesize powders with higher electron densities. The determined electron density of C12A5S4 is greater than the theoretical maximum electron density of C12A7 electride, which suggests successful doping of silicon into aluminum sites of the mayenite cages. It also relies on the fact that silicon caused the cages' overall charge to increase, resulting in more electrons needed to satisfy electroneutrality.
Table 2.1 Theoretical & determined electron densities of mayenite electride synthesized via the sol-gel method, aluminothermic method & silicon doped mayenite electride

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical Maximum Electron Density (e⁻/cm³)</th>
<th>Determined Electron Density via Iodometry (e⁻/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C12A7e⁻ via Sol-gel, C12A7:O²⁻ precursors</td>
<td>2.33×10^{21}</td>
<td>2.36×10^{20}</td>
</tr>
<tr>
<td>C12A7:e⁻ via Sol-gel, CA &amp; C3A precursors</td>
<td>2.33×10^{21}</td>
<td>3.68×10^{20}</td>
</tr>
<tr>
<td>C12A7:e⁻ via Aluminothermic</td>
<td>2.33×10^{21}</td>
<td>1.25×10^{21}</td>
</tr>
<tr>
<td>C12A6S2:e⁻</td>
<td>3.50×10^{21}</td>
<td>2.12×10^{21}</td>
</tr>
<tr>
<td>C12A5S4:e⁻</td>
<td>4.66×10^{21}</td>
<td>3.82×10^{21}</td>
</tr>
</tbody>
</table>

In conclusion, just based on the characterization of the powders synthesized from the various methods, it can be said that the aluminothermic method is superior to the sol-gel method. The aluminothermic method creates phase pure mayenite electride powders with higher electron densities than the sol-gel route. As well, the silicon doped synthesis results in electride powders with even higher electron densities. The use of C12A5S4 would be preferable over C12A6S2 due to the higher electron density of C12A5S4 and one less phase impurity compared to C12A6S2. To apply these materials in a permeation test, one would instinctively use mayenite electride powders synthesized via the aluminothermic method and use C12A5S4 as the silicon doped comparison. The material must have a high electron density and be able to form a fully dense membrane to fabricate a hydrogen-permeable membrane.
CHAPTER THREE
FABRICATION AND TESTING OF THE HYDROGEN PERMEABLE MEMBRANE

This final chapter focuses on the fabrication of dense mayenite membranes as well as their hydrogen permeation testing. Arguably, one of the most important properties of the membrane is that it should be dense enough to prevent non-hydrogen gas diffusion through the membrane to ensure hydrogen selectivity. Thus, the cornerstone in the fabrication of the membrane is to achieve a dense membrane. The phase inversion method was of interest due to the possibility of preparing a thin, dense membrane on a porous substrate. The mayenite pellets fabricated by phase inversion method from the sol-gel and aluminothermic methods were characterized using scanning electron microscopy (SEM). The dual-pressing method was the next method used to fabricate the mayenite membranes. SEM characterization was also performed to investigate the microstructures for membranes fabricated from powders by different synthesis methods. The addition of a sintering aid to a dual pressed membrane was investigated in order to increase the density of the membrane. The hydrogen permeation testing procedures & apparatus are outlined and explained. Challenges faced for the mayenite-based hydrogen-permeable membranes are described. Conclusions are to be drawn according to the fabrication method and SEM results. Lastly, the future work that should be done on this topic is discussed.
3.1 Phase Inversion Method

The phase inversion method is an effective ceramic processing method used to prepare a thin dense membrane on a porous substrate. **Figure 3.1** describes the general membrane structure resulting from the phase inversion method. A thin dense layer can act as the functional layer for selective hydrogen permeation. The intermediate layer having small pores provides a transition layer to allow the defect-free top functional layer’s deposition, without introducing too high of a gas permeation resistance. The bottom layer having many big pores provides enough mechanical support to the membrane without noticeable gas permeation resistance. Therefore, this membrane configuration is exactly what the mayenite-based hydrogen-permeable membrane should be.

![Figure 3.1 Structure of a ceramic membrane fabricated through phase inversion](image)

We tried to fabricate the mayenite membrane using this phase inversion method. The C12A7:O2− oxymayenite powders synthesized via the sol-gel method were added to an organic solution containing N-methyl-2-pyrrolidone (NMP), polyethersulfone (PES),
and polyvinyl pyrrolidone (PVP) to form a slurry. The slurry was ball-milled for 24 hours using 3mm YSZ balls. A thick layer was tape-casted on a plastic sheet and submerged in water for 24 hours. During the submersion in water, the NMP in the layer was exchanged with water. After that, circular and rectangular pieces were punched out from the sheet generated in tape casting. The resulting pieces were then dried at 180°C in a box oven. It was thought that the thickness of the full layer would affect the thickness of the dense layer. Therefore, the effect of the full layer thickness of the green membrane was investigated. The thickness of the layer can be changed in tape-casting using the doctor blade. The full green layer thickness was set to be 1.1mm, 1.3mm, and 1.5 mm. Figure 3.2 provides the photos of the oxymayenite membranes with variable thicknesses after drying. All the membranes look the same without cracks or curvature formed because of drying. The cross-section of one membrane was characterized using optical microscopy. The optical microscope image, shown in Figure 3.3, shows that the big straight pores were formed in the bottom support layer (e.g., the region is outlined by the red line). A relatively dense layer was present at the top of the membrane. However, it was also found that small holes still existed in the top layer (e.g., the red circle on the figure identifies a hole penetrating the dense layer). Figure 3.3 demonstrated that the phase-inversion could achieve the desired gradient structure comprising porous support layers and a relatively dense layer. However, the existing holes may result in a problem for the future densification during the high-temperature sintering step.
Figure 3.2 Phase inverted samples pre-sintering

Figure 3.3 Optical microscope image of a cross-section of a phase inverted pellet, pre-sintering
The dried oxymayenite samples derived by the phase inversion method samples were sintered at 1300 °C for 12 hours in a box furnace in an ambient environment. It was observed that after sintering, the pellets had become warped and distorted. The distortion of the pellets can be seen in Figure 3.4. In addition to the warping of the pellets, the pellets also wholly lacked any mechanical strength. With a light touch, the pellets would crack and disintegrate. Therefore, the phase inversion method was decided not currently suitable to fabricate dense membranes for hydrogen permeation using C12A7. Additional work could be completed in the future to optimize this method to achieve a fully dense membrane & support with good mechanical strength.

Figure 3.4 Phase inverted pellets after sintering at 1300 °C for 12 hours

3.2 Fabrication of Pellets from Aluminothermic & Silicothermic Powders

3.2.1 Aluminothermic Pellet Fabrication

Due to the high electron density of powders resulting from the aluminothermic synthesis of mayenite electride, it is desirable to fabricate the dense membranes for hydrogen permeation from these powders. In addition to the high electron density, these
powders are also desirable to use, due to the one-step reaction method compared to the multi-step sol-gel synthesis method. In this section, the procedure used to fabricate the pellets is to be described. The issues of using these powders are also to be discussed.

Initially, the powders were dry-pressed utilizing a hydraulic uniaxial pellet press in a stainless circular die. It was found that the pellets would not shape well and would crack after they were released from the die. Due to this failed pressing, it was decided that the powders needed a binding aid. One of the most commonly used binders in the lab group was a 5% PVA aqueous solution. However, when using this binder, the PVA would then be burned out during sintering. After sintering, the regions that contained PVA would now be porous. This porosity could be enough to allow the diffusion of non-hydrogen gases. Therefore, pure water was chosen as a binder. After 1-2 drops of water were added, the powders were ground and pressed. It was found that water was sufficient to allow the powders to shape well enough to be sintered. However, there was one concern with using water. It has been demonstrated by Dong et al. [23] that when mayenite electride was exposed to water, it reacted with water by forming impure phases of \( \text{Ca}_3\text{Al}_2(\text{OH})_{12} \) and \( \text{Al}(\text{OH})_3 \). This degradation process of mayenite powders and pellets in 100% humidity is shown in Figure 3.5. The white dots apparent in the electride pellet, and the color change of the powders from dark green to bright green demonstrated the degradation. During the pellets’ pressing, the amount of water binder was far less than the amount of water used to study C12A7:e\(^-\) stability in our previous work. The pellets exposed to water were much shorter because the as-pressed pellets were put into a furnace to dry for 10 hours. Therefore,
the effects of the water binder would be much less than that in the study by Dong et al. The pellets were pressed using 12 MPa of uniaxial force and afterward sintered at 1350 °C for 12 hours utilizing a 2°C/minute ramp rate.

![Figure 3.5](image)

**Figure 3.5** (A) Electride powders resting in 100% humidity (B) Electride pellet submerged in water [23]

After sintering, the resulting mayenite pellets’ microstructure was studied using a scanning electron microscope (SEM) Hitachi SU6600. Before the SEM investigation, a thin platinum layer was coated on the sample surface through a sputter coater for
preventing the buildup of charge on the surface of the sample during SEM operation. The mode chosen for image collection was secondary electrons due to the interest of the material’s porosity on the surface. As seen in Figure 3.6 and Figure 3.7, these pellets are not fully dense. The top surface is very porous, and the cross-sectional image also displays many gaps in the structure that would allow non-hydrogen gases to diffuse through the membrane. Therefore, it is difficult to obtain fully dense mayenite electride pellets from aluminothermic mayenite electride powders through the simple dry-pressing method.

Figure 3.6 Top surface view of a C12A7:e⁻ pellet prepared from aluminothermic powders, sintered at 1350 °C for 12 hours
3.2.2 Silicothermic Pellet Fabrication

Since silicon doped mayenite electride powders were synthesized, it was also desirable to see if they could form a dense membrane for hydrogen permeation. Since the objective of synthesizing a silicon doped mayenite was to increase the electron density, the sample containing the highest electron density was used, which was C12A5S4. This ratio was also used over C12A6S2 due to the presence of CA in C12A6S2. To form a membrane for permeation testing, these powders were ground using a mortar and pestle, and pressed into a pellet using 12 MPa of uniaxial pressure with the addition of 1-2 drops of water as a binder. The resulting pellets were sintered at 1350°C for 12 hours in a tubular furnace. A temperature ramp rate of 2°C/minute was used to reduce the pellets’ thermal stresses to avoid cracking. Since these pellets were to be used as a possible hydrogen-permeable
membrane, the sintering environment was studied for two different batches of C12A5S4 powders. This was done to make sure that C12A5S4 could also be a mixed electron and proton conductor. One batch was sintered in a 100% argon environment, while the other batch was sintered in 5% H₂ 95% Ar. An interesting phenomenon about the pellet’s color distribution could be seen after sintering, as indicated in Figure 3.8 and Figure 3.9. Five mayenite electride pellets were sintered in the same batch as positioned in Figure 3.8. The arrow shows the protection gas flow direction in Figure 3.8. It can be seen that the pellets near the gas inlet exposed to the gas earlier had become much whiter than the pellets far from the gas inlet exposed to the gas later. The pellets near the gas inlet have the most exposure to the hydrogen and formed mayenite hydride with white color explain this observation. It is also noticeable that some of the powders have come off from the pellet. It can also be seen more drastically for the mayenite pellets sintered in an argon atmosphere (Figure 3.9). The outgassing of the pellets could cause this during sintering. Since margarite was a phase present in the pellets, there may be a reaction occurring that releases oxygen and hydrogen in CaAl₂(Al₂Si₂)O₁₀(OH)₂. After polishing, it was found that the bulk of the pellets retained black coloring, as seen in Figure 3.10. To be sure that the pellets sintered in 5% hydrogen had not changed in bulk, a pellet was cracked into half and is shown in Figure 3.11. It can be seen that the interior of the pellet remained black after sintering, indicating the gas flow effect only occurred on the surface of the mayenite electride pellets.
Figure 3.8 C12A5S4 pellets after sintering in 5% H₂ 95% Ar, the arrow represents the direction of the gas flow

Figure 3.9 C12A5S4 pellets after sintering in argon
Figure 3.10 C12A5S4 pellets sintered in argon after polishing

Figure 3.11 Cross-section view of a C12A5S4 pellet after sintering in 5% H$_2$ 95% Ar & cracking in half
SEM characterization was used to investigate if these pellets were fully dense. Figures 3.12 and 3.13 show the SEM images of the C12A5S4 pellet sintered in argon. Figure 3.12 shows that big pores exist on the pellet surface. The majority of the surface is relatively dense or has small pores. Figure 3.13 shows that the whole cross-section of the pellet is very porous. Two kinds of morphologies exist. The well-sintered regions formed a connected network and large pores. The less-sintered regions were surrounded by the network and showed a relatively dense structure or less small pores. Figures 3.14 and 3.15 provide the SEM characterization for the pellet sintered in 5% hydrogen 95% argon. This pellet is not at all any better than the pellet sintered in argon. The pellet surface and cross-section show a similar microstructure as that of the mayenite electride pellets sintered in argon. However, the general relative density improved to some degree, although it was still very porous.

![SEM characterization image](image-url)

**Figure 3.12** Top surface view of a C12A5S4 pellet sintered in argon
Figure 3.13 Cross-sectional view of C12A5S4 pellet sintered in argon

Figure 3.14 Top surface view of a C12A5S4 pellet sintered in 5% H₂ 95% Ar
In conclusion, both aluminothermic and silicothermic powders were not successful in creating fully dense membranes based on the SEM imaging present. In future work, experiments could be developed to find better sintering conditions that would allow for fully dense pellets fabricated from the aluminothermic and silicothermic powders.

3.3 Fabrication of Thin Films with the Help of Sintering Aids

It has been shown by Dong et al. [23] that one could fabricate fully dense pellets from C12A7 mayenite oxide powder and CA+C3A mixture powder synthesized using the sol-gel method, as seen in Figure 3.16. However, there are still a few small pores in the membranes. In this section, we attempted to further increase the membrane’s relative
density by adding the sintering aids of NiO and Fe$_2$O$_3$. These dopants were chosen based on the literature on sintering aids for various ceramics. NiO is an effective sintering aid used in the proton conducting ceramic BCZY [27, 28, 29]. Therefore, it was chosen as a candidate sintering aid for densifying C12A7. Fe$_2$O$_3$ is also an effective sintering aid for densifying yttrium-stabilized zirconia [30,31] C12A7 [32], where the addition of iron resulted in the lowering of the crystallization temperature. Therefore, Fe$_2$O$_3$ can also serve as a sintering aid for achieving a fully densified C12A7 membrane. The amount of dopant for NiO and Fe$_2$O$_3$ was kept constant at 1wt% of the C12A7. The green pellets were dry-pressed out of the resulting CA+C3A powders from the sol-gel method. Sintering took place at 1350 °C for 12 hours in a flowing argon environment, which allowed the fabrication of densified mayenite pellets.

**Figure 3.16** (a) Pellet fabricated from C12A7 powders after a graphite reduction at 1400°C for 6 hours (b) Pellet fabricated from CA & C3A powders after a graphite reduction at 1400°C for 6 hours [23]
The resulting pellets were examined by SEM imaging. Figure 3.17 shows the cross-section of the pellet resulting from the addition of 1wt% NiO. The red circles highlight pores. The addition of NiO appeared to induce more porosity in the sample rather than help densification. The increase in porosity could result from the reaction between C12A7 and nickel oxide. Figure 3.18 shows the cross-section of the pellets resulting from the addition of 1wt% Fe₂O₃. Fe₂O₃ addition fabricated mayenite pellets with much fewer pores than the pellet with NiO as a sintering aid. Therefore, in the following work, thin dense membranes would be synthesized using CA+C3A as a precursor with 1wt% Fe₂O₃ as a sintering aid.

Figure 3.17 Cross-sectional image of C12A7 pellet sintered with 1 wt% NiO as a sintering aid
3.4 Co-pressing Fabrication of a Thin Membrane

It is better to fabricate thin and dense membranes for achieving high hydrogen permeation. It is essential to fabricate the thin and dense membrane on a thick, porous support layer because the membrane with a thickness of only several tens of micrometers is mechanically weak and is easily cracked with handling. It was found by Xia et al. [26] that co-pressing was a suitable method to fabricate dense ceramic membranes on porous substrates. This section focused effort on co-pressing different powders’ layers to fabricate a thin and dense membrane on a porous support layer. Powders obtained from the sol-gel method were utilized to co-press pellets of a thin dense layer and a supporting porous layer.

Figure 3.18 Cross-sectional image of C12A7 pellet sintered with 1 wt% Fe₂O₃ as a sintering aid
The use of CA+C3A mixture powder was chosen for introducing a dense layer for the membrane as it has shown excellent sinterability in our previous study. The mixture of 30wt% percent mixture of starch and 70wt% oxymayenite powder synthesized by the sol-gel method served to introduce the porous support layer. During the sintering, it is expected that the starch burns out, leaving behind pores to allow gas to diffuse to the dense membrane. Initially, only one support layer was used to support the dense membrane. It was found that the dense membrane would often end up cracked because of asymmetric structure. A dual support symmetric structure with a dense thin membrane sandwich between two porous support layers was created (Figure 3.19 b) to solve this problem. A supporting layer was first pressed using 6 MPa of uniaxial pressure, then powder with better sinterability was added to the top of the first supporting layer and was further pressed again at 6 MPa. Lastly, the second supporting layer of the powder mixed with starch was added onto the dense layer while still in the die and pressed one last time using 12 MPa. The membranes with the sandwiched structure were sintered at 1350 °C for 12 hours with a ramp rate of 2 °C per minute. A comparison between the traditional method and the sandwich method is shown in Figure 3.19 b. The sandwiched membrane structure can protect the thin layer from cracking and introduce the thinner dense layer. The packing of particles, in the visualization in Figure 3.19 a, shows that the thin layer for the traditional method is a 3 particle-layer thick membrane, while the sandwich method can result in a thin layer with a 2 particle-layer thick membrane, using the same number of particles for the membrane. Based on this understanding, it is possible to achieve a thinner dense
membrane utilizing the sandwich structure. Thus, all membranes were fabricated using the sandwich structure.

**Figure 3.19** (a) A comparison between having 1 layer to support and two supporting layers (b) A sandwich structure created by the co-pressing of powders

Two different sandwich pellets were fabricated. Both pellets utilized the C12A7 oxymayenite powder from the sol-gel method with 30wt% starch as the supporting layers. The difference between the two pellets lies within the dense layer. One pellet used a mixture of CA+C3A from the sol-gel method, while the other pellet used 1wt% iron oxide as a sintering aid in the dense membrane layer in addition to the CA+C3A mixture powder. Comparing **Figure 3.20** and **Figure 3.21**, the SEM images of the two pellets’ cross-sections show no drastic difference between the microstructure of the dense layers. In both layers, very few pores are present. There is no significant increase in density by using Fe$_2$O$_3$ as a dopant. It was possible to achieve a dense layer of 40-60 µm using this co-pressing method. Considering **Figure 3.22**, it is evident that the top support layer is porous enough to allow gas to diffuse to the thin, dense membrane. Fe$_2$O$_3$ has been found [33] to change the geometrical and electronic structure of mayenite. Therefore, it is better to use pure
mayenite rather than Fe₂O₃ assisted mayenite due to the effects of Fe₂O₃ on the conduction of electrons and protons through a thin, dense layer.

Figure 3.20 Cross-sectional image of the sandwich structure resulting from the addition of 1wt% Fe₂O₃ to the dense layer

Figure 3.21 Cross-sectional image of the sandwich structure resulting from CA+C3A without the addition of Fe₂O₃
In conclusion, co-pressing a sandwich structure from CA+C3A precursors for the dense layer and C12A7 mixed with 30% starch for the two porous support layers is the best candidate to test the permeation of hydrogen through the dense membrane.

3.5 Hydrogen Permeation Performance Testing

Now that the membrane fabrication has been completed, the final step after sintering is the reduction of the oxymayenite phase present in the pellets into mayenite electride. To create a mixed ionic and electronic conductor, the reduction environment of
5% H₂+ 95% Ar was used. The sandwich-structured pellet was placed in graphite powders and was reduced at 1400°C for 6 hours. To test the performance of the hydrogen permeation membrane, the pellet was sealed onto the top of an alumina tube and placed in a quartz tube. Pure H₂ gas was supplied in the quartz tube at a rate of 100 ml per minute. A smaller alumina tube was placed inside the alumina tube that the pellet was sealed on to provide a sweep gas to the bottom of the pellet. This sweep gas consisted of 5% H₂ and 95% Ar flowing at 20 ml per minute to provide a concentration gradient between the top and bottom of the pellet. A schematic of the set-up is shown in Figure 3.23. The initial test was performed at 800 °C due to the higher conductivity of mayenite electride at elevated temperatures. After reaching the desired temperature, a test was performed to ensure the pellet was not leaking any gasses. To do this, a mass spectrometer (MS) was used to analyze the permeate gas. Helium would be introduced into the upper chamber and the permeate gas would be sent to the mass spectrometer.

Initial testing was conducted, and it was found that the pellet was correctly sealed, no helium was detected in the mass spectrometry results. To determine the permeation flux in the preliminary result, a flowmeter was used. The pure hydrogen gas inlet and outlet were tested with the flow meter. A difference of -5.1 ml per minute was found between the inlet and outlet of the pure H₂ chamber. The permeate gas inlet and outlet was also tested with the flow meter. It was found that the inlet measured at 20 ml per minute and the outlet had increased to 25.1 ml per minute. Since it was previously found that the pellet was not leaking any gas, it could be concluded that the pellet was indeed permeating gas through a
dense layer. The resulting H₂ flow was found to be 5.1 ml per minute. The effective flux is the flow divided by the effective area. The effective area was found to be 1.13 cm². Thus, the effective flux is 4.51 ml/minute/cm². This flux can also be written as 3.319×10⁻⁶ moles/cm²/s. Compared to hydrogen permeation through metallic membranes, which range from 10⁻⁴ to 10⁻¹ moles/cm²/s [34], permeation through this mayenite electride membrane is approximately 2 orders of magnitude less than that of some metallic membranes. It is worth noting that the operating temperature of this ceramic membrane can be as high as 900°C, which is several hundred degrees higher than that of some metallic membranes. In other ceramic membranes such as one based on a dual phase barium, cerium, and iron compound (BCF), permeation flux was found to be 0.76 ml/minute/cm² at 950°C [6]. The permeation result found in this work for mayenite electride is more than 4 times higher than that of the dual-phase BCF ceramic.
The objective was to repeat the preliminary results and analyze the flow using mass spectrometry at a range of temperatures ranging from 500-800°C. However, further trials after the initial all resulted in leaking of the pellet after the temperature was elevated to 800°C. The initial sealing used was a glass powder sealant that was applied by mixing the glass powders with a small amount of water until a viscous slurry was formed. Repeated use of this sealing resulted in repeated leaking of the testing apparatus. Another type of sealant was tried, ceramabond 552. This sealing is a commercially available sealant used for alumina applications. The use of ceramabond 552 also caused cracking which can be

**Figure 3.23** Schematic diagram of the testing apparatus used to test the hydrogen permeation performance
seen in Figure 3.24. In part (c) of Figure 3.24, it can be seen that bubbles formed on the inside of the ceramabond sealant, which was thought to be one of the causes of leaking through the pellet. To combat this, a layer of glass powder would be applied to the pellet followed by a layer of ceramabond. However, this also resulted in gas leakage through the pellet after elevating the temperature. Referring to Figure 3.25, the bottom of the image is of the porous pellet while the top shows the sealant. It is apparent that small cracks in the micrometer range also form in addition to the large cracks seen with the naked eye. This was the major challenge faced that could not be resolved. The cracking in the pellet and sealant is due to the mismatch of the coefficient of thermal expansion between the pellet, alumina tube and sealant.
Figure 3.24 (a) Multiple cracking in the sealant (b) Cracking in the sealant that propagates into the pellet (c) Bubble formation on the inside of the sealant (d) Cracking of the sealant that propagated under the pellet

Figure 3.25 Microcracks in the sealant demonstrated in the top of the image
3.6 Conclusions & Future Work

In this work, mayenite electride powders have been successfully synthesized by various methods, resulting in different properties. A silicon doped mayenite electride was synthesized and was shown to have increased electron density, which is desirable for the permeation of hydrogen. Sintering aids were investigated to increase the density of a membrane, but it was found that the sintering aids did not provide much improvement and could affect the permeation results. Methods were investigated to fabricate a thin, self-supported, dense membrane and a successful method was found. Preliminary performance testing results revealed that mayenite electride was able to permeate hydrogen through a thin, self-supported, dense membrane. However, repeating the initial result failed due to constant cracking of the membrane & sealant.

Future work on this topic should focus on determining a method that will seal the sandwich structure pellet onto the alumina tube without cracking. Once this has been achieved, repetition of the initial permeation result should be obtained. Analysis via mass spectrometry should be completed to achieve a more accurate hydrogen flux through the membrane. This can be achieved by running known concentrations of hydrogen and argon mixtures through the mass spectrometer and creating a calibration curve of concentrations. Then the permeate gas can be plotted on the calibration curve to determine the actual concentration of hydrogen present in the permeate gas. Permeation testing should be performed at 50°C increments from 500-800°C. Insight into the permeation can be gained
through conductivity tests of mayenite electride utilizing electrochemical impedance spectroscopy. Further work can be done to find a method to create dense pellets of C12A5S4 to test the hydrogen permeation of the silicon doped sample to confirm that increased electron density would result in increased hydrogen permeation. Conductivity tests can be performed on the C12A5S4 sample to confirm that the increased electron density resulting from the substitution of silicon atoms into aluminum sites does indeed increase the conductivity, and the increase in conductivity could be related to the hydrogen permeation results.
References


Published Work

