

Yttria stabilized zirconia membrane stability in molten fluoride fluxes for low-carbon magnesium production by the SOM process

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Abstract: The Solid Oxide Membrane (SOM) process for magnesium production is a technology that involves the direct electrolysis of magnesium oxide for energy efficient and low-carbon magnesium production. In the SOM process, magnesium oxide is dissolved in a molten ionic flux comprised of a CaF_2 - MgF_2 eutectic mixture. An oxygen-ion-conducting SOM tube, made from yttria stabilized zirconia (YSZ), is submerged in the flux. The operating life of the electrolytic cell can be improved by understanding degradation processes in the YSZ membrane, and one way in which the membrane degrades is by yttria diffusion out of the membrane. By adding small amounts of yttrium fluoride to the flux, yttria diffusion can be limited and controlled. The diffusion of yttria into the flux was quantified by determining the yttria concentration profile as a function of immersion time in the flux and distance from the flux-membrane interface. Yttria concentrations were determined using energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS). The diffusion process was modeled using a numerical approach in conjunction with an analytic solution to Fick's second law. These modeling and experimental methods allowed for the determination of the optimum yttrium fluoride concentration in the flux to minimize yttria diffusion and improve membrane stability. Furthermore, the effects of certain impurities commonly found in magnesium ores, such as calcium oxide, silica, and sodium oxide/sodium peroxide, on membrane stability are also being investigated under static and potentiodynamic conditions.

Keywords: Magnesium, Solid oxide membrane, SOM, YSZ, Diffusion

1. Introduction

Magnesium is the third most abundant metal in the earth's crust, and the world's production of magnesium is expected to increase 7% per annum¹. Automobile manufacturers want to increase the amount of magnesium used in automobiles from 5kg per vehicle to 40-100kg per vehicle because magnesium has the lowest density of all structural metals. Magnesium's low mass and high strength to weight ratio makes it an ideal candidate for replacing aluminum and steel in vehicles; magnesium is 78% lighter per unit volume than steel and 36% lighter per unit volume than aluminum². For automakers to use magnesium as a steel replacement, however, the magnesium to galvanized steel cost ratio must be 4.33:1. Further, for automakers to use magnesium as an aluminum replacement, the magnesium to aluminum cost ratio must be 1.8:1³. The magnesium-steel cost ratio was 8:1, and the magnesium-aluminum cost ratio was 2.5:1 in 2008.

The Solid Oxide Membrane (SOM) process has been successfully employed for the low-carbon production of magnesium on a laboratory scale⁴. The results from laboratory operation of the SOM process for magnesium were extrapolated, and the SOM process is expected to meet the demand for low cost primary magnesium production due to minimum pre-processing, low capital costs, small manufacturing plant size, and low energy costs. The environmental friendliness of the process makes it even more attractive³.

The SOM process for magnesium production operates by dissolving magnesium oxide (MgO) in a molten fluoride based flux comprised of a eutectic mixture of calcium fluoride (CaF₂) and magnesium fluoride (MgF₂) at 1190°C. The flux with dissolved MgO is held in a type 304 stainless steel chamber, and a one-end-closed, oxygen-anion conducting SOM tube is submerged into the flux. The SOM tube is made from yttria stabilized zirconia. The stainless steel wall of the electrolysis chamber acts as the cathode, and a liquid metal anode is placed inside the SOM tube. When an electric potential is applied across the electrolysis cell, oxygen anions are transported through the flux and the YSZ tube to the liquid metal anode inside the SOM tube, where oxidation occurs; simultaneously, magnesium cations move through the flux to the solid stainless steel cathode, where reduction occurs.

The YSZ membrane acts as a solid electrolyte in the SOM electrolysis process, as it separates the cathode and flux from the anode; under an applied potential oxygen anions travel from the cathode through the YSZ to the anode where they are oxidized. The stability of the YSZ membrane is thought to be the limiting factor in the operating life of a SOM electrolysis cell. A study by Krishnan suggested that one means of membrane degradation is yttria (Y₂O₃) diffusion from the YSZ membrane to the flux⁴. No previous study, however, has reported on the long term stability of the YSZ membrane in the flux. Further, the SOM process has been studied in significant detail in a laboratory environment, operating under ideal conditions with high purity fluxes. The effect of flux impurities on membrane stability has never before been investigated. This study aimed to quantify and model the yttria diffusion process and develop a preliminary understanding of the effects of flux impurities on YSZ membrane stability.

2. Experimental

2.1 Static Experiment Details, without Impurities

Static experiments were performed to quantify the yttria diffusion rate out of YSZ membranes in which no electric potential was applied across the membranes. These experiments were executed by submerging 5 cm sections of open ended YSZ tubes, supplied by McDanel Ceramics, into 2.5 cm of molten flux of varying composition at 1190°C. All YSZ tubes had a 1.91 cm outer diameter, a 1.27 cm inner diameter, and an yttria content of 10.5w%. An alumina extension rod was attached to the membranes using alumina paste, supplied by Aremco, so that the membrane could be submerged into the flux from above. The molten salt fluxes were held in open, type 304 stainless steel crucibles, with an outer diameter of 4.45 cm, an inner diameter of 4.11 cm, and a height of 12.7 cm. A drawing of the experimental set-up is shown in Figure 1.

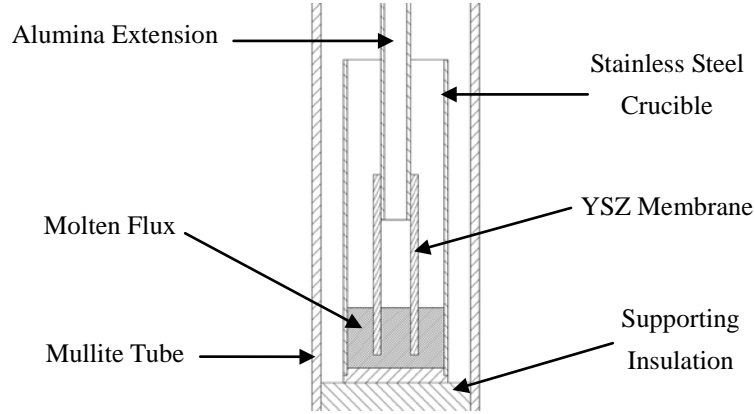


Figure 1: Static experiment set-up

The compositions of the molten fluxes tested, without impurities, are shown in Table 1. The flux constituents, magnesium fluoride hydrate, 96% pure magnesium oxide, 99.5% pure calcium fluoride, and 99.99% pure yttrium fluoride, all supplied by Alfa Aesar, were dried for 12 hours at 250°C to remove moisture from the salts. After drying, the powders were mixed at 200 rpm in Nalgene bottles for 2 hours on a ball mill. 100 grams of mixed powder was poured into the stainless steel crucibles. The crucibles with the powder were then placed into a tube furnace and heated to 1190°C at a rate of 4°C/min in an atmosphere of 5% hydrogen and 95% argon to prevent corrosion of the stainless steel. The hydrogen-argon gas mixture was continually passed through the experiment at a rate of 300 cm³/min. Membranes were not submerged into the molten fluxes until the experimental set-up temperature equilibrated at 1190°C for 1 hour. Once submerged, membranes stayed in the flux for a total of 16, 24, 32, or 100 hours before being raised out of the flux and cooled at 4°C/min.

Table 1: Flux compositions tested in static experiments, without impurities

w% YF3	w% CaF2	w% MgF2	w% MgO
0	40.5	49.5	10.0
1.6	39.8	48.6	10.0
2.0	39.6	48.4	10.0
5.0	38.3	46.8	10.0

2.2 Static Experiment Details, with Impurities

The compositions of the molten fluxes tested with impurities are shown in Table 2, and the impurities tested were calcium oxide (CaO), silica (SiO₂), and sodium oxide/sodium peroxide (Na₂O/Na₂O₂), which are common impurities found in magnesium oxide. The concentrations of impurities tested in the flux were determined based upon the projected operation of the SOM electrolysis over thousands of hours; as magnesium oxide will be continually added to electrolysis cells, the concentration of impurity in the flux will increase due to impurities found in magnesium oxide. The impurity concentrations tested were upper estimates on the total impurity concentrations present in the flux at any given time. 96% pure calcium oxide, 99.9% pure silica, and sodium oxide/sodium peroxide powders, supplied by Alfa Aesar, were added to the flux powders and processed as described in the previous section of this paper. Experiments with impurities underwent the same experimental procedure, heating rate, and gas flow conditions as experiments

without impurities with the exception of the experiment with silica. Only argon gas was passed through the system at 300 cm³/min, without hydrogen, to prevent formation of silicon tetrafluoride gas. In all impurity experiments, YSZ membranes were submerged in the flux for 32 hours before being raised out of the flux and cooled at 4°C/min.

Table 2: Flux compositions tested in static experiments, with impurities

w% YF ₃	w% CaF ₂	w% MgF ₂	w% MgO	w% Impurity
2.0	37.4	45.6	10.0	5% CaO
2.0	38.7	47.3	10.0	2.0% SiO ₂
2.0	38.7	47.3	10.0	2.0% Na ₂ O/Na ₂ O ₂

2.3 Electrolysis Experiment Details

Four experiments were performed in which magnesium was produced in order to test the membrane stability during electrolysis with: 1) No YF₃ added to the flux, 2) YF₃ added to the flux, 3) CaO impurity, and 4) Na₂O/Na₂O₂ impurity. Figures 2 and 3 show the design of the SOM electrolysis cells used in these experiments. The electrolysis cells had an upper electrolysis chamber which was heated to 1190°C, where dissociation of MgO took place, and a lower condensing chamber which was maintained in a temperature range of 1050°C to 300°C, where condensation of magnesium gas took place. The cells were constructed from type 304 stainless steel and heated to the previously mentioned temperatures at a rate of 4°C/min. The cathode was the stainless steel cell wall, and the anode was a bath of liquid silver metal inside the one-end-closed, 1.27 cm inner diameter YSZ membrane. In experiments without impurities, a 6.35 mm outer diameter molybdenum tube was used as the anode current collector. Hydrogen gas was passed at 60 cm³/min through the molybdenum tube into the silver to lower the magnesium oxide dissociation potential and prevent oxidation of the molybdenum tube. In experiments with impurities, a solid graphite rod was used as the anode current collector. The outside of the electrolysis cell was held in a reducing atmosphere of 5% hydrogen and 95% argon at 300 cm³/min to prevent corrosion of the stainless steel. Meanwhile, argon was passed at a flow rate of 300 cm³/min into the electrolysis chamber through the annulus between the YSZ membrane and the stainless steel tube extending out of the top of the upper chamber. The argon gas carried magnesium vapor into the condensing chamber and lowered the magnesium vapor pressure to prevent reduction of the YSZ membrane. In all experiments with YF₃ in the flux, argon gas was also stirred into the flux to maintain a homogenous flux mixture during electrolysis. Magnesium vapor exited the electrolysis chamber through two stainless steel tubes that extended from the condensing chamber into the electrolysis chamber, protruding above the flux. H₂O_(g) produced at the anode exited through an alumina tube attached to the YSZ membrane with alumina paste, supplied by Aremco. The compositions of the molten fluxes tested during electrolysis experiments are shown in Table 3.

Table 3: Flux compositions tested during electrolysis experiments

w% YF ₃	w% CaF ₂	w% MgF ₂	w% MgO	w% Impurity
0	40.5	49.5	10.0	0.0%
2.0	39.6	48.4	10.0	0.0%
2.0	37.4	45.6	10.0	5% CaO
2.0	38.8	47.4	10.0	1.8% Na ₂ O/Na ₂ O ₂

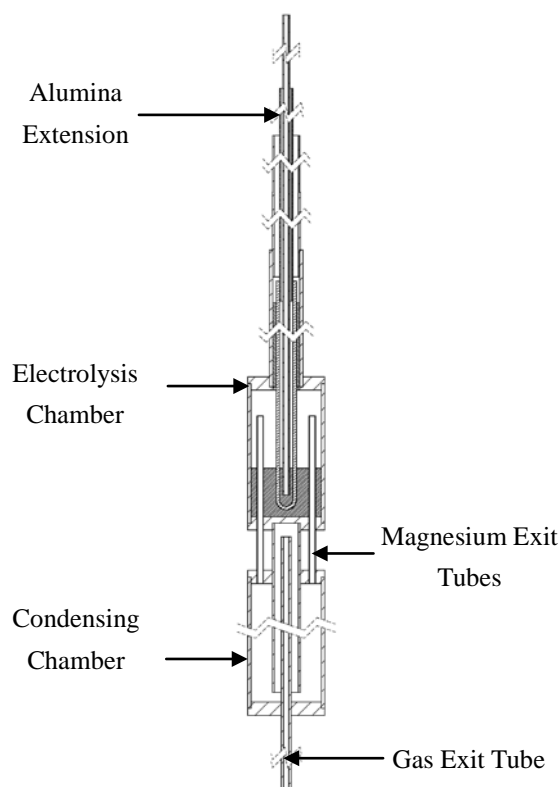


Figure 2: Front view of electrolysis cell

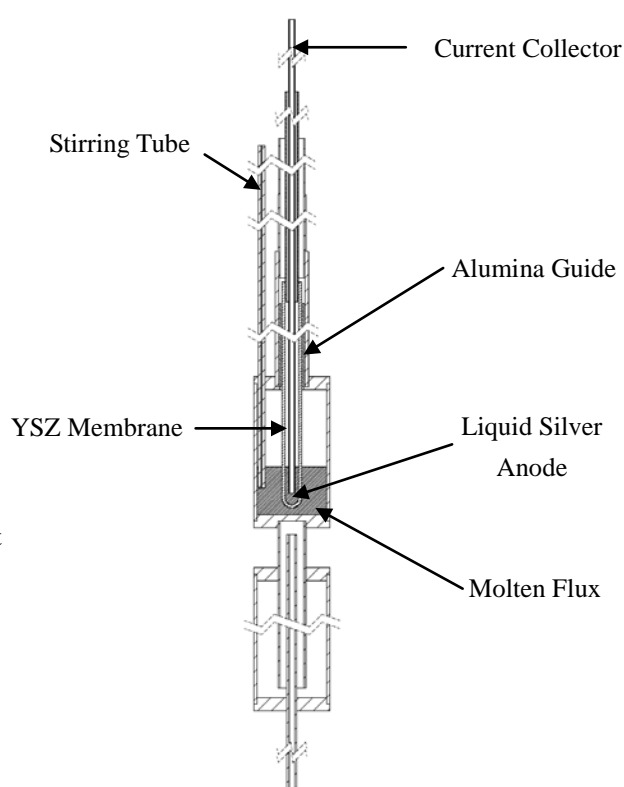


Figure 3: Right view of electrolysis cell

2.4 Sample Preparation and Analysis

All membrane samples were prepared for analysis by first sectioning the YSZ membranes 0.25 cm above the lowest point of submersion using a diamond saw. These YSZ sections were then mounted in an epoxy resin. The samples were allowed to dry under vacuum for 1 hour, and then dry for 12 hours more at room temperature. The samples were then prepared using grinding and polishing steps: 1) 45 micron diamond grinding, 2) 30 micron diamond grinding, 3) 15 micron diamond grinding, 4) 6 micron diamond polishing, 5) 3 micron diamond polishing, 6) 1 micron diamond polishing, 6) 0.25 micron diamond polishing. A carbon coating was applied to the surface of the polished membrane sample by sputtering, and energy dispersive spectroscopy (EDS) or wavelength dispersive X-ray spectroscopy (WDS) was performed in order to determine oxide concentrations in the membranes.

3. Results

3.1 Static Experiments, without Impurities

Figure 4 shows an image of a membrane exposed to the flux for 32 hours in a static experiment with no YF_3 present. Figure 5 shows a membrane as received from the manufacturer. Figure 6 shows a membrane sample that was exposed to 2.0w% YF_3 in the flux for 100 hours. Note that in all membrane images shown in this paper, the membrane bulk is depicted on the left, and the flux-membrane interface is on the right. During static experiments with no impurities in the

flux, 32 hour experiments yielded a 60 micron diffusion zone originating at the flux-membrane interface and extending into bulk of the membrane. The diffusion profiles of yttria in the membranes, obtained from WDS analysis, are shown in Figure 7 for the first 160 microns of the YSZ membrane. In the four trials shown, each diffusion profile approaches the membrane bulk yttria concentration of 10.5w%.

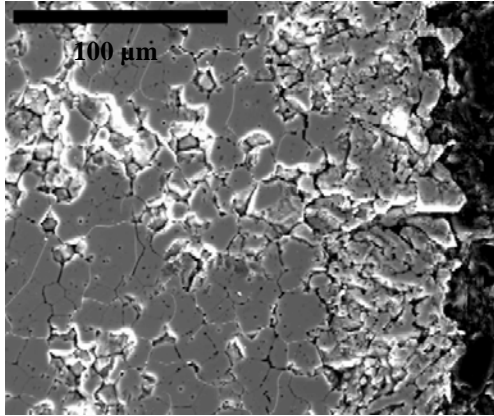


Figure 4: Membrane exposed to flux (32 hours)

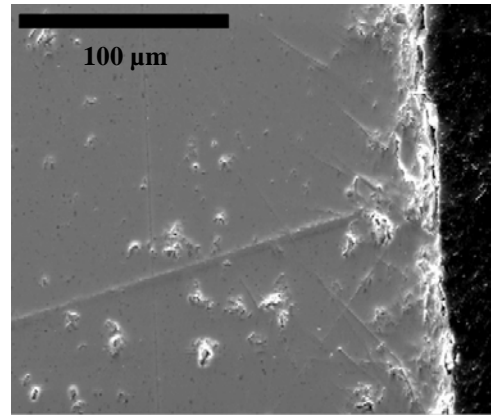


Figure 5: Membrane as received from manufacturer

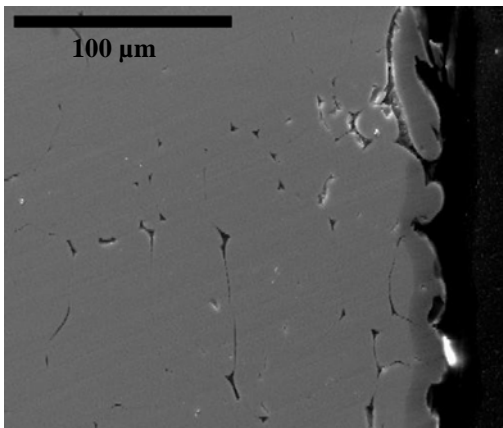


Figure 6: Membrane exposed to 2w% YF_3 (100 hours)

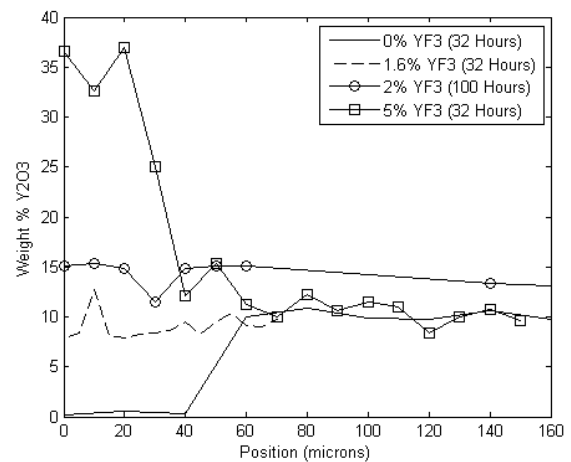


Figure 7: Yttria concentration profiles

3.2 Static Experiments, with Impurities

Figures 8, 9, and 10 show membrane samples exposed to CaO , SiO_2 , and $\text{Na}_2\text{O}/\text{Na}_2\text{O}_2$ impurities for 32 hours, respectively. The yttria and zirconia (ZrO_2) profiles as a function of position are shown in Figure 11 for the first 80 microns of the YSZ membrane. The data shown in Figure 11 was obtained from WDS analysis. No significant amounts of CaO , SiO_2 , or $\text{Na}_2\text{O}/\text{Na}_2\text{O}_2$ were found in the membranes.

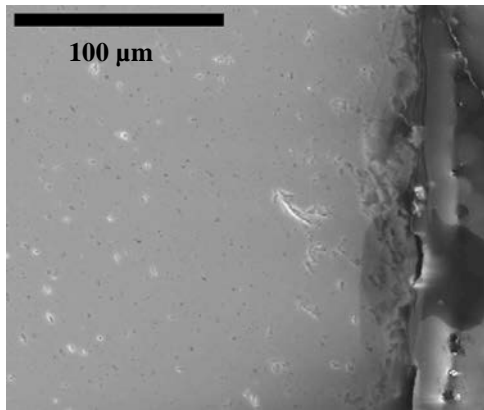


Figure 8: Membrane exposed to CaO impurity

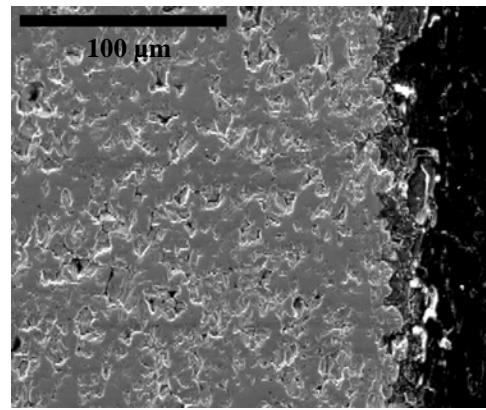


Figure 9: Membrane exposed to SiO₂ impurity

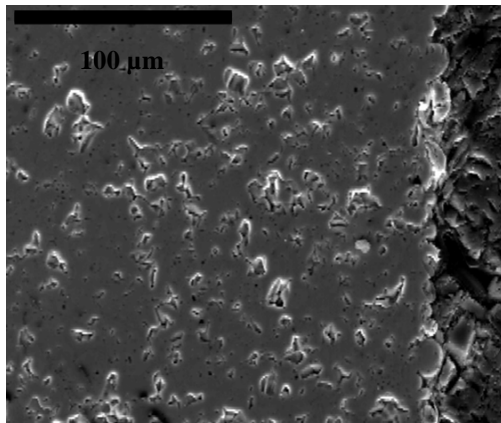


Figure 10: Membrane exposed to Na₂O/Na₂O₂ impurity
Profiles

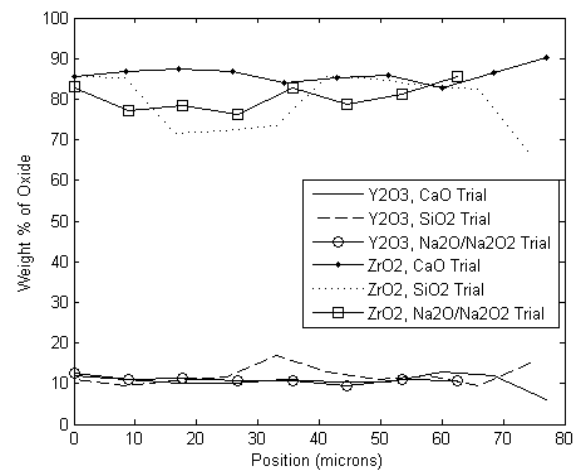


Figure 11: Y₂O₃ and ZrO₂ Concentration

3.3 Electrolysis Experiments

A YSZ membrane was exposed to flux for 23 hours in an electrolysis experiment in which magnesium oxide was dissociated to produce magnesium metal. 9600 coulombs were passed through the electrolysis cell. EDS analysis was performed on this membrane sample, and the yttrium concentration profile is shown in Figure 12. Also in Figure 12, the yttrium profile found via EDS analysis for a 24 hour static experiment is included for comparison. In each experiment, no YF₃ was added to the flux. Another membrane was exposed to 2.0w% YF₃ in the flux during an electrolysis experiment, and the yttria profile was found to be constant throughout the membrane.

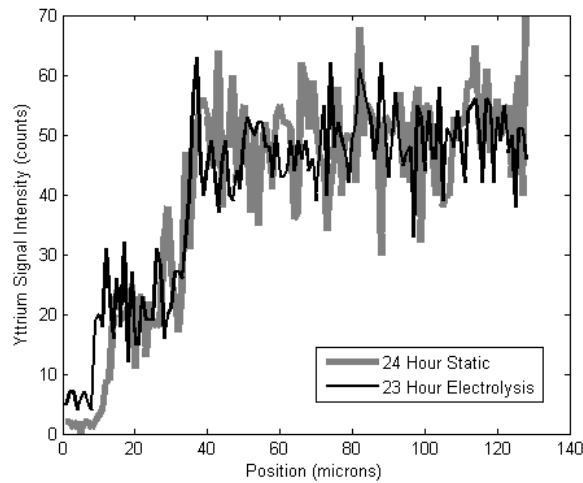


Figure 12: Yttrium concentration profiles for static and electrolysis experiments with no YF_3

Membranes exposed to CaO and $\text{Na}_2\text{O}/\text{Na}_2\text{O}_2$ during electrolysis experiments are shown in Figures 13 and 14, respectively. Both membranes exhibited constant yttria and zirconia profiles which were obtained by WDS and EDS.

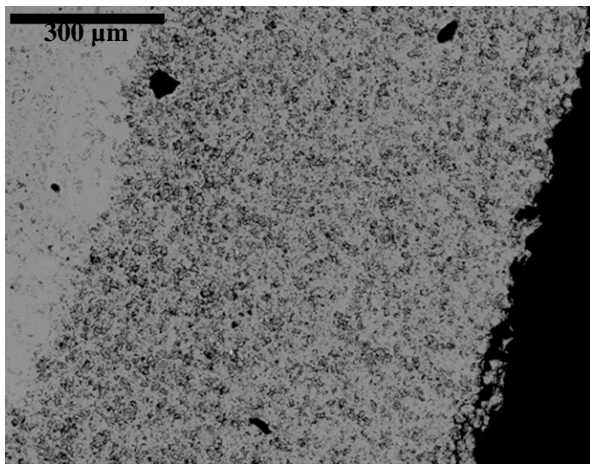


Figure 13: Membrane after electrolysis with CaO

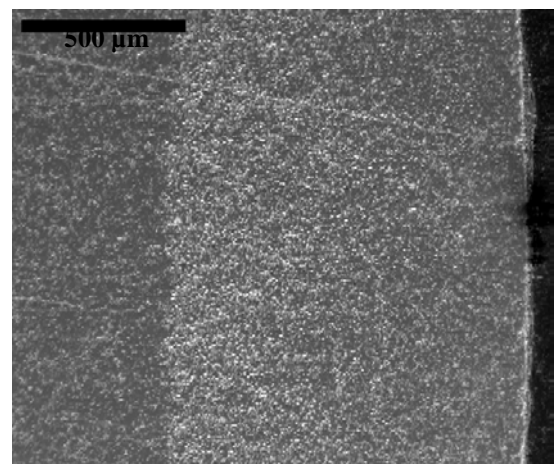


Figure 14: Membrane after electrolysis with $\text{Na}_2\text{O}/\text{Na}_2\text{O}_2$

4. Discussion

4.1 Yttria Diffusion

The change in membrane composition as a function of position and YF_3 concentration in the flux can be attributed to a chemical diffusion process. By varying the YF_3 concentration in the flux containing MgO , the activity of yttria in the flux can be adjusted to match the activity of yttria in the YSZ membrane, halting the diffusion process. Additionally, when the concentration of YF_3 in the flux is sufficiently high, the activity of yttria in the flux can be made greater than the activity of the yttria in the YSZ membrane. Therefore, yttria concentration in the membrane could increase due to diffusion of yttria into the membrane from the flux; yttria concentration in the YSZ membrane decreased when the

activity of yttria in the flux was lower than that of the YSZ membrane.

The yttria concentration profile as a function of position in a membrane exposed to a flux with YF_3 was modeled using the semi-infinite solution to Fick's second law. The semi-infinite boundary condition was assumed to begin at the flux-membrane interface and extend into the bulk of the membrane. This solution is shown in Equation 1, where C_0 is the steady-state concentration at the flux-membrane interface, C_∞ is the bulk concentration in the membrane, x is position, t is time, and D is the diffusivity of yttria in the membrane⁵.

Equation 1:

$$C = C_0 + (C_\infty - C_0) * \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

The diffusivity of yttria in the membranes was determined using a least squares numerical approximation by fitting the experiment data to the semi-infinite diffusion model. This method yielded a diffusivity value of $D = 5.6 \times 10^{-11} \text{ cm}^2/\text{s}$. A comparison of the experimental and modeled diffusion profiles for the 32 hour, 5% YF_3 flux concentration experiment is shown in Figure 15. The diffusion model did not hold for the case when no YF_3 was present in the flux because the high porosity causes the flux to flow into the membrane and deplete the yttria from the exposed surface of the membrane. A step function diffusion profile, rather than an error function, was seen in the 0% YF_3 case, shown in Figure 7.

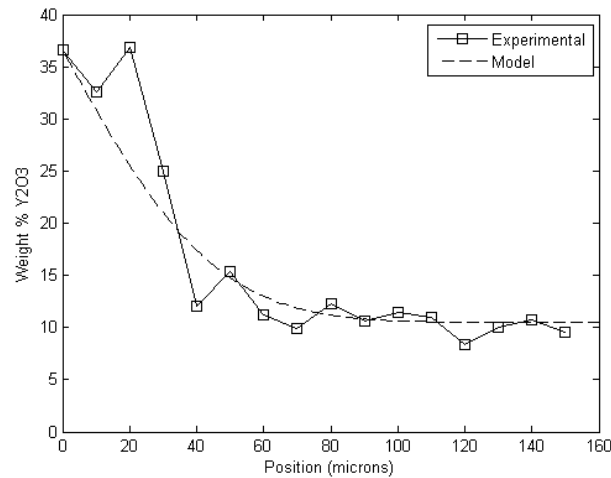


Figure 15: Yttria concentration profile for a membrane exposed to 5.0w% YF_3 in the flux for 32 hours

The YSZ membrane will never reach the C_0 value shown in Equation 1 during SOM electrolysis operation, but determining the C_0 value was important because it allows for prediction of the yttria concentration in the YSZ near the flux-membrane interface. A change in yttria concentration in the membrane could lead to changes in the structural and ion-conducting properties of the YSZ. Changing the structure could lead to weakened mechanical strength, and decreasing the oxygen-ion-conductivity could lower the overall efficiency of the SOM electrolysis cell.

Prior studies have offered insight to a range of acceptable yttria concentrations for SOM electrolysis operation.

Mechanically, the membranes are most stable when both tetragonal and cubic phases are present, and these phases are metastable in the range of 5 to 16.5mol% yttria⁶. The main purpose of considering mechanical stability of the membrane is to maintain the original phase of the membrane provided by the manufacturer. The SOM tube is suspended in the flux and external forces are never applied, so increasing its mechanical strength is not a concern. Considering the oxygen anion conductivity, maximum conductivity occurs at approximately 8.6mol% yttria⁷. Although the YSZ membrane accounts for a significant portion of the SOM electrolysis cell resistance, small changes in ion conductivity will change the overall cell resistance negligibly. Literature values suggest that compositional changes in the range of 8.6 to 15mol% yttria would account for less than a 1% increase of the cell resistance. It has been decided the optimum yttria concentration range should be no lower than the manufacturer's concentration and no higher than 15mol% yttria. This optimum range corresponds to a 10.5 to 24.4w% yttria composition.

Using the data at the flux-membrane interfaces shown in Figure 7, a linear function was developed to describe the steady-state interfacial composition of the YSZ membranes as a function of YF₃ concentration in the flux. The linear function was obtained using a least squares numerical approximation and is shown in Equation 2. In Equation 2, C_F is the weight percent concentration of YF₃ in the flux.

Equation 2:

$$C_0 = 7.9665C_F - 2.9842$$

Using Equation 2 to predict yttria concentration in membranes as a function of YF₃ concentration in the flux and considering the range of acceptable yttria concentrations leads to a range of YF₃ concentrations that can be added to the flux. This range has been determined to be 1.7 to 3.4w% YF₃. Within in this range, 2.0w% YF₃ in the flux has been tested for 100 hours and offers the best control of yttria diffusion in experiments to date. This concentration has been chosen as an ideal concentration for SOM electrolysis operation, maintaining mechanical and conductive properties as well as producing an yttria profile in membranes that closely matches the manufacturer's composition.

4.2 Impurities

The effects of three different impurities, calcium oxide, silica, and sodium oxide/sodium peroxide on YSZ membranes were tested during static experiments for 32 hours. In each of these experiments, the optimum 2.0w% YF₃ concentration was added to the flux to eliminate chemical diffusion of yttria as a degradation pathway. The zirconia and yttria profiles were fairly constant in the CaO trial, but the membranes exposed to SiO₂ and Na₂O/Na₂O₂ showed erratic zirconia concentration profiles. In each membrane, the impurity concentration was less 1% at any position. The 1% impurity concentration falls within the error of the WDS analysis and therefore is not quantitatively valid.

Calcium oxide has a minimal effect on membrane stability. Membranes show constant zirconia and yttria profiles, and the porous region of the membrane was only 20 microns long. Further, calcium oxide (calcia) is commonly used as a stabilizing agent in zirconia. Diffusion of calcia into the YSZ membrane would create calcia-yttria stabilized zirconia (CaYSZ) which can exhibit ion conductivity comparable to YSZ⁸. Calcium oxide exhibited no corrosive behavior on the membrane. Calcium oxide will be the most abundant flux impurity in an industrial SOM process and is of negligible

concern with respect to membrane degradation. Future studies should consider the viability of the CaO impurity as an additional membrane stabilizer in the flux, possibly reducing the need to add YF_3 to the flux. Studies have shown high CaO diffusivity into YSZ, making CaO a plausible stabilizer⁹.

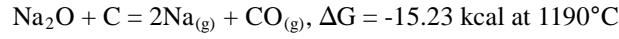
SiO_2 and $\text{Na}_2\text{O}/\text{Na}_2\text{O}_2$ impurities were found to cause degradation to the membranes by increasing membrane porosity. The porosity increase was much greater in the membrane exposed to SiO_2 than $\text{Na}_2\text{O}/\text{Na}_2\text{O}_2$. The increased porosity was possibly caused by zirconia degradation; the zirconia concentration profiles in the membranes were erratic, suggesting a correlation between severe porosity increase and zirconia degradation. It appears that the membrane degradation was due to a corrosive process. More investigation is required to verify the degradation pathway, but regardless of the degradation mechanism, the silica impurity significantly degraded the membrane in a static experiment.

4.3 Electrolysis Experiments

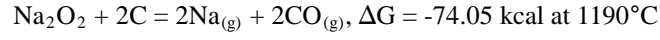
An electrolysis experiment was performed for 23 hours with no YF_3 added to the flux. This experiment has been compared to a static membrane experiment in which a membrane was submerged in the flux for 24 hours with no YF_3 added to the flux. The yttrium profiles shown in Figure 12 are nearly identical, suggesting that the yttria diffusion process is independent of the applied potential during electrolysis. Chemical diffusion is therefore believed to be the primary method of yttria migration from the YSZ membranes, and applied potential does not play major role in this process. A prior study by Monceau, Filal, Petot, and Petot-Ervas predicted that an applied electric potential across YSZ would cause no recognizable demixing of yttria¹⁰. An electrolysis experiment in which 2.0w% YF_3 was added to the flux also showed no signs of increased yttria migration, further supporting the theory that applied potential has no effect on yttria diffusion. In electrolysis experiments without impurities present in the flux, membranes showed a porous region of approximately 1000 microns; the large porous region is believed to have been caused by electronic current in the cell providing another membrane degradation pathway. Electronic current is thought to degrade the YSZ membrane by electrochemical reduction, and this degradation pathway is currently being investigated in a new study.

Electrolysis experiments performed with CaO and $\text{Na}_2\text{O}/\text{Na}_2\text{O}_2$ impurities in the flux yielded membranes with constant yttria and zirconia concentration profiles. Yttria diffusion was stopped due to the addition of YF_3 in the flux. The membranes did exhibit increased porosity when compared to static experiments. In both the impurity electrolysis experiments, the membrane's porous region extended approximately 1000 microns. In the static experiments the porous region in the CaO experiment extended 20 microns, and the porous region in the $\text{Na}_2\text{O}/\text{Na}_2\text{O}_2$ experiment extended 200 microns into the membrane. The increased porous region is believed to be caused by the presence of electronic current in the cell, as previously discussed. The impurities are not believed to be the primary cause of this large porous region. Further, the electrolysis experiment with $\text{Na}_2\text{O}/\text{Na}_2\text{O}_2$ impurity yielded a sodium hydroxide hydrate deposit in the condensing chamber. The composition of the deposit was determined using X-ray diffraction. The deposit suggests that the sodium ions were removed from solution due to spontaneous reactions, shown in Equations 3 and 4, subsequently removing the negative effects of the impurity on membrane stability¹¹.

Equation 3:



Equation 4:



4.4 Statistical Confidence

The percent error of the quantitative WDS analysis was quantified by comparing the theoretical yttria weight percent provided by the manufacturer to the yttria weight percent measured in a new membrane sample as received from the manufacturer. The theoretical yttria weight percent provided by manufacturer specifications was 10.5w%. The theoretical weight percent, measured weight percent, and percent error are plotted as a function of position in Figure 16. The maximum percent error measured was 24.4%, and the average percent error measured was 13.6%.

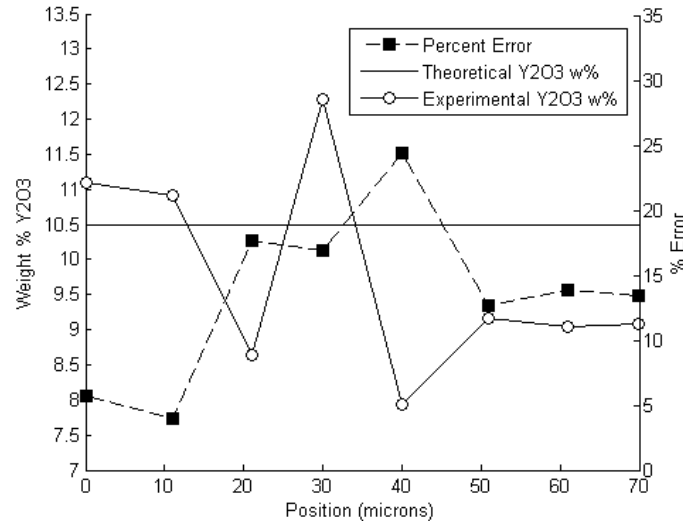


Figure 16: Percent error analysis for WDS method

5. Conclusions

Yttria diffusion has been confirmed as a method of membrane degradation in the SOM process for magnesium production. The diffusion process can be controlled by introducing a small concentration of yttrium fluoride to the CaF_2 - MgF_2 molten flux. 2.0w% YF_3 concentration in the flux has been accepted as the optimum YF_3 concentration for electrolysis cell operation, but it has been predicted through a model of the diffusion process that a concentration range of 1.7 to 3.4w% YF_3 in the flux would be acceptable for the SOM process. The diffusivity of yttria in the YSZ membranes was determined to be $5.6 \times 10^{-11} \text{ cm}^2/\text{s}$. More membrane samples will be tested to confirm the validity of the diffusion model and value of the diffusivity constant. Also, degradation by yttria diffusion was found to be a process independent of applied potential during electrolysis.

The effects of certain impurities, CaO , SiO_2 , and $\text{Na}_2\text{O}/\text{Na}_2\text{O}_2$, have been preliminarily investigated. CaO poses no threat to membrane stability, whereas SiO_2 and $\text{Na}_2\text{O}/\text{Na}_2\text{O}_2$ have been shown to increase membrane porosity by a degradation mechanism that must be investigated further. $\text{Na}_2\text{O}/\text{Na}_2\text{O}_2$ impurity should not present an issue if the

condensing chamber temperature is tightly controlled because sodium gas spontaneously removed from solution will condense in a discrete region of the condensing chamber. Degradation due to SiO_2 was so significant in experiments that it is recommended to avoid its presence in the flux.

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