

SCALING-UP SOLID OXIDE MEMBRANE ELECTROLYSIS TECHNOLOGY FOR MAGNESIUM PRODUCTION

Soobhankar Pati¹, Adam Powell¹, Steve Tucker¹, Steve Derezinski¹

¹Metal Oxygen Separation Technologies; 11 Michigan Drive, Natick, MA, 02114, USA

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Abstract

Metal Oxygen Separation Technologies, Inc. (MOxST) is actively developing Solid Oxide Membrane (SOM) electrolysis technology for production of magnesium directly from its oxide. The vital component of this technology is the oxygen ion-conducting solid zirconia electrolyte separating the molten flux (a mixture of salts and oxide) and the inert anode. The zirconia not only protects the anode from the flux but also prevents anode gas back-reaction, increasing the efficiency. This makes it possible to produce low-cost high-purity magnesium and high-purity oxygen as a by-product with no direct greenhouse gas emissions. In this paper we discuss the design modifications made to address the scaling-up challenges, particularly for producing magnesium in liquid form. The key accomplishment to date is the successful development of a prototype capable of producing few kilograms of magnesium per day. We will also describe the prerequisite properties of an inert anode and suitable materials for the same.

Introduction

Automakers are keenly looking for appropriate lightweight materials to increase fuel efficiency and decrease greenhouse gas emission. It is estimated that the efficiency of automobiles can be increased ~1% by reducing the automobile mass by 22.5kg (1). Magnesium with a density of 1.74 g/cm³, about 30% and 75 % less than aluminum and steel respectively, is a suitable material for replacing steel and aluminum. Along with its low density, its high stiffness-to-weight ratio makes it an ideal candidate to replace some the structural components of automobiles without compromising safety. It is also potentially the most easily recycled of the proposed light weight vehicle materials, which include polymers and composites. Further benefits of magnesium include lower manufacturing cost and reduced noise, vibration, and harshness. For these reasons, automakers would like to replace 350 kg of steel and aluminum alloy parts per vehicle with 160 kg of magnesium equivalents by the year 2020. This would improve fleet fuel economy by about 1.5 mpg and reduce petroleum demand by over \$20 billion per year (2).

Currently, automobiles are made with only few magnesium components, such as bumper support beams, steering support column, and seat/channel guide etc., averaging ~6 kg/car. However, the amount of magnesium used in automobiles is projected to increase with additional applications such as the engine cradle, sub-frame, and body components. As mentioned before, around 160 kg of magnesium is expected to be used in a typical automobile. This will create a huge demand for magnesium. In 2010 approximately 60 million automobiles were produced. If the magnesium content of autos were to increase to 160kg per vehicle, the auto industry will require 9.6 million metric tons. This is almost 10 times the 2010 primary magnesium

production. If automakers are to meet these goals, primary magnesium producers will have to scale up their production capacity considerably. This new demand will mandate novel, energy-efficient and disruptive primary magnesium production technologies as the present technologies are very inefficient and not environmentally benign (3).

Solid Oxide Membrane (SOM) electrolysis is such a novel, efficient technology that can produce magnesium at fraction of its present cost (4). The SOM electrolyzer consists of a one-end closed, dense, cubic-phase stabilized zirconia tube immersed in a molten salt bath. It is operated by feeding magnesium oxide into the molten salt bath and applying potential across the cathode, immersed in the molten salt bath and the anode, encased inside the one-end closed zirconia tube. The electricity splits magnesium oxide to produce magnesium metal vapor at the cathode and oxygen gas at the anode. A detail description of the process is given elsewhere (4-5).

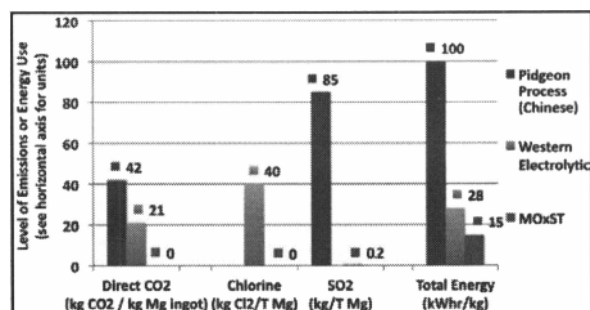


Figure 1. Energy usage and greenhouse gas emission of different primary magnesium production technologies.

Figure 1 shows comparison of the energy usage and greenhouse gas emission of different primary magnesium production technologies (3, 6). The SOM process generates minimal waste compared to other processes. The amount of energy required for per kg is also considerably lower compared to the other processes. It can be operated in modular electrolysis cells, enabling small production facilities at very low capital cost, minimizing startup risks.

In this paper we discuss the recent developments towards scaling up the SOM electrolysis process from producing a few grams per day to a few kilograms per day of magnesium. Nearly all the previous studies report on single-tube SOM electrolyzers. Here we present the results of a scaled-up SOM electrolyzer with three zirconia tubes. We compare results of a three-tube and single-tube

SOM electrolyzer. It is very critical to understand the modularity before scaling up SOM electrolyzer technology. Also, to date SOM electrolysis technology for magnesium production used a reducing environment at the anode. This enabled the operation of the SOM electrolyzer with a metallic current collector at the anode. However, in a commercial system where oxygen is produced at the anode, an oxygen stable current collector is needed for continuous, uninterrupted operation. Towards that, this paper presents some preliminary studies on a suitable design and materials system.

Design and Experiments

Set-up- Figure 2 shows photographs of fabricated welded stainless steel crucible-condenser reaction vessel assemblies for one and three-tube experiments. Except for one experiment where we used 5/16" SS-304 tubes as isolated cathodes, the vessel containing the molten salt served as the cathode for both single-tube and three-tube electrolyzers. The 1" outer diameter (OD) and 7/8" inner diameter (ID) stainless tubes rise from the crucible to the retort top plate surrounding the zirconia SOM tubes and sealing them at the top plate. We used 1/4" ID stainless tubes descending from the retort top plate down into the crucible to stir the molten flux electrolyte with argon. The MgO is fed through the 3/8" OD 1/4" ID stainless tube rising from the crucible top to the retort top plate. The argon and magnesium vapor in the crucible was carried to the condenser through the 1/4" OD tubes connecting crucible to the condenser. Since the condenser is at a cooler temperature than the crucible, the magnesium vapor condensed on the wall of the condenser and the argon gas exited through the 1/4" tubes connected to condenser.

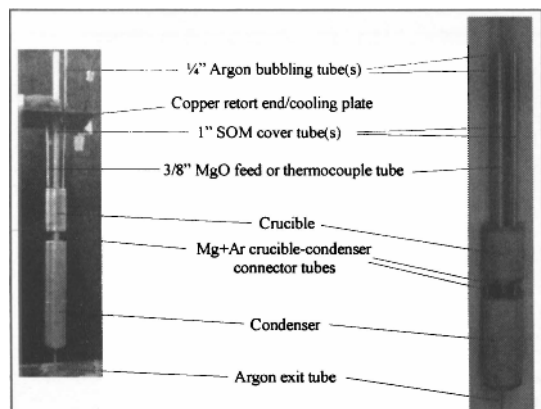


Figure 2. Stainless steel welded reaction vessel for SOM Electrolysis: one-tube vessel on left, three-tube vessel on right.

We used 10 wt% MgO content in the molten salt mixture for all of the electrolysis experiments. The molten salt was composed of either 50wt % $\text{CaF}_2\text{-MgF}_2$ or 50wt % $\text{CaF}_2\text{-MgF}_2$ with a required amount of YF_3 . We used commercially purchased yttria stabilized zirconia (YSZ) tubes (OD: 0.75", ID: 0.5") for the experiments. The MgF_2 , CaF_2 , YF_3 and MgO were purchased from Alfa Aesar. We heated the SOM electrolyzer in an inert, low oxygen environment to prevent the weld joint failure from oxidation. We maintained the inert environment by heating the SOM electrolysis cell inside a mullite or a quartz tube and flushed with argon into the tube. The water cooled aluminum flanges sealed

with silicone O-rings maintain the inert environment inside the quartz tube.

Current Collector- In all of the previous studies liquid copper or tin with a carbon rod current collector or a liquid tin with molybdenum tube current collector were used as anodes (4,5,7). In the first case carbon acted as a reductant while in the second case hydrogen gas was supplied through the molybdenum tube as a reductant. However, this only works if we are not interested in producing oxygen at the anode. When oxygen is generated at the SOM electrolyzer, the anode is expected to behave as the cathode of solid oxide fuel cell (SOFC). Therefore, a perovskite such as lanthanum strontium manganite (LSM), which is a SOFC cathode material, is an obvious choice. However, since the operating temperature of the SOM electrolyzer is around 1150°C, it is expected that the LSM will sinter within a short duration and may delaminate if operated at higher current density.

One way to get around this problem would be to use a liquid metal that is stable in an oxygen environment. Liquid silver is one such promising candidate. Figure 3 (left) shows the assembly with a liquid metal anode and current collector immersed in it. The current collector, as indicated in Figure 3, must provide an electrical connection from the anode to the power supply, while functioning in a pure oxygen environment from room temperature to the operating temperature. Also it should have an extremely low solubility in the liquid anode. Iridium satisfies all of these requirements, but is inordinately expensive.

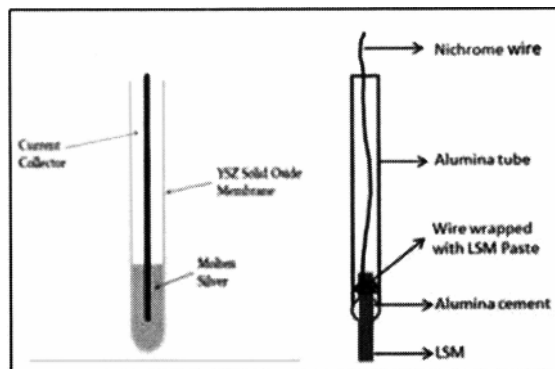


Figure 3. Assembly with liquid metal anode and current collector (left). LSM/ Nichrome current collector (right).

It is also possible to use metals that form a thin protective oxide scale which can conduct electricity. Therefore, we tested nichrome and almel for some experiments expecting they would form a thin protective oxide layer which might be conductive. Figure 3 (right) shows the design of another current collector used for some experiments. It consists of a ceramic electronically conducting oxide like, LSM immersed in the liquid silver. The LSM is attached to a nichrome wire and the nichrome wire is protected by an alumina tube and alumina cement as shown in Figure 3 (right).

Results and Discussion

Figure 4 shows a potentiodynamic scan before electrolysis when nichrome current collector was used in the anode of a single-tube electrolyzer. The current density was around 0.7 A/cm² at 4 V.

The scan shows a reasonably clean sweep with very low current below 1.5 V. The change in slope at 1.5 V is due to dissociation of MgO and formation of metal at the cathode. This is a representative scan for most experiments when a reductant is used at the anode. It is hypothesized that the nichrome oxidizes at the anode to lower dissociation potential of MgO, which would be around 2.3 V when pure oxygen is generated at the anode.

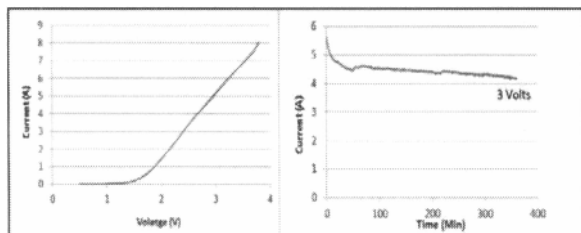


Figure 4. Potentiodynamic scan prior to electrolysis (left), electrolysis at 3 V for 6 hrs (right).

Figure 4 (right) shows the current-time plot during electrolysis. It shows a steady decrease in current with time. This is most likely due to decrease in MgO content in the flux. Figure 5 shows the 304 stainless steel shim which served as a condenser liner, with magnesium deposits. Due to the temperature gradient of the furnace heating zone the top of the shim was at higher temperature than the bottom of the shim. Therefore, the undercooling is greater at the bottom of the shim and the magnesium vapor deposited as fine flaky particles. The metal which condensed at the top of shim collected as liquid magnesium globules (Figure 5), indicating that it is possible to produce liquid magnesium in a SOM electrolysis process. However, proper condenser design is vital to produce a fully-liquid magnesium product.



Figure 5. Metal deposit on stainless shim (left).

In order to explore the process efficiency, we used gas fittings to connect the oxygen output to an oxygen sensor and flow meter. Figure 6 shows the current measured, oxygen output of the SOM tube during three brief electrolysis runs experiment, scaled such that they align under Faradaic conditions, i.e. perfect current efficiency. During the first electrolysis run, oxygen output indicates perfect current efficiency after a brief delay, which we believe to be due to oxygen buildup in the liquid silver anode. During the second and third, however, current efficiency is somewhat lower. One possible reason for change in current efficiency may be electronic conduction in the flux. During

electrolysis, the magnesium metal product has a tendency to dissolve in the flux, especially when it forms at atmospheric pressure away from argon.

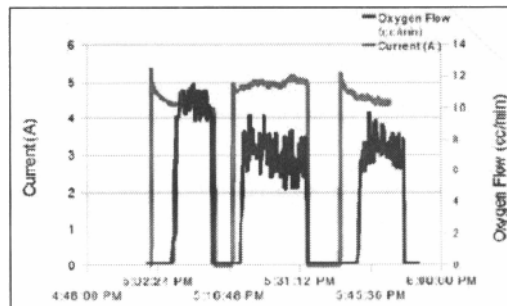


Figure 6. Current and scaled oxygen output during electrolysis.

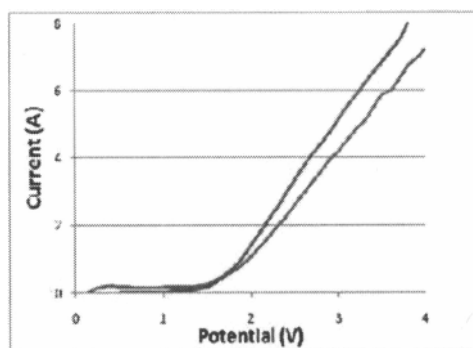


Figure 7. Potentiodynamic scans before (red) and after (blue) electrolysis.

Figure 7 compares potentiodynamic scans before and after electrolysis. The potentiodynamic scan after electrolysis (blue line) shows onset of a small “leakage current” prior to dissociation potential of MgO. This leakage current lowers the current efficiency. Eric et. al., in the abstract titled “Effect of Electronic Current on the SOM Process for Magnesium Production” to be presented in Electrometallurgy 2012 at TMS 2012, give a detail explanation of the origin of the leakage current and how it can be eliminated.

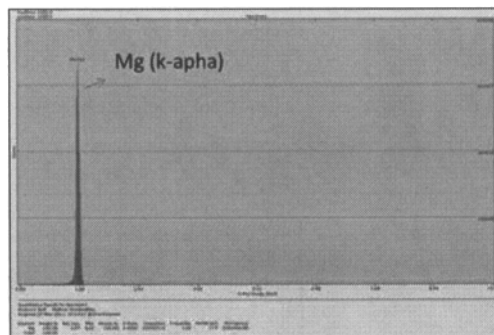


Figure 8. EDAX spectrum of magnesium deposit, showing no detectable impurities.

Figure 8 shows the energy-dispersive X-ray (EDAX) spectrum of the magnesium deposit from this experiment. EDAX can detect elements at 0.1% concentration, so the spectrum and analysis indicate that this magnesium is at least 99.99% pure. This is because this process features in-line distillation, enabling it to make high-purity magnesium from moderate-purity MgO.

Figure 9 shows the typical current-potential characteristics of the three-tube SOM electrolyzer with similar immersion depth as the single-tube experiment. The linear portion of the curve intersects the horizontal axis at about 1.5 V similar to single-tube electrolyzer experiments. It should be noted at any given potential the current is approximately 3 times of the current in a single-tube electrolyzer.

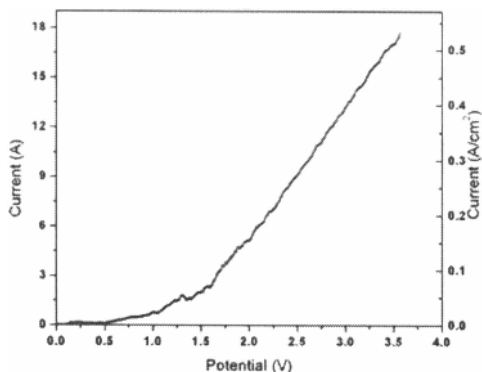


Figure 9. Potentiodynamic scan of the 3-tube apparatus, showing both total current and current density.

After this characterization step, the apparatus ran for one hour at a fixed potential of 3 V to produce magnesium. Figure 10 shows the current during this potentiostatic hold. Current begins at 12A and then decreases to around 9.5A over about 10 minutes as oxide ions are depleted from the zirconia/salt boundary layer. The 9 A current level then slowly falls as the oxide ion concentration in the flux decreases over time.

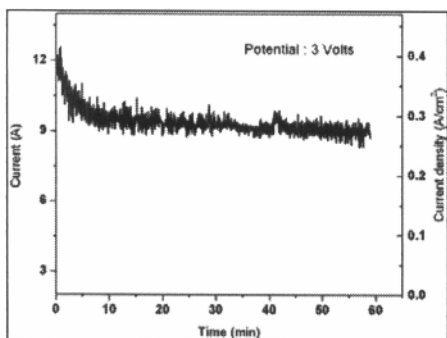


Figure 10. Current variation over time during a 3V potentiostatic hold.

In order to produce tens of tons of magnesium per year, electrolysis cells must be scaled up by increasing both the number of zirconia tubes and the immersion depth of each tube in the molten salt. This will increase the electrode area and total current. We conducted a single-tube deep-immersion experiment. Around

3.5" of the tube was immersed in molten salt during the experiment. Figure 11 shows the comparison of the potentiodynamic scans of a typical shallow-immersion experiment and a single-tube deep-immersion experiment. The potentiodynamic scan of the deep-immersion experiment (blue line) shows a reasonably clean sweep with little current below the dissociation potential of 1.5 V. When compared to a single tube shallow-immersion experiment it can be seen that the current is nearly twice as high for the deep-immersion experiment. This is consistent because electrode area of the deep immersion experiments is approximately twice that of shallow immersion experiments.

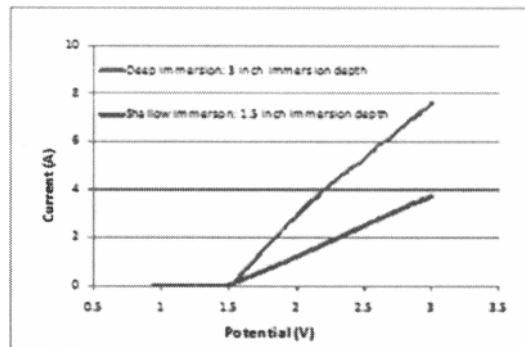


Figure 11. Potentiodynamic scan comparison of deep and shallow immersion experiments; right: deep immersion current.

We built a three-tube SOM electrolyzer which can contain around 8.0 kg of salt and MgO mixture. This electrolyzer is capable of accommodating up to 10" immersion depth, providing large electrode surface area on each tube. The combined electrode area for three tubes is approximately 240 cm² with an 8" immersion depth. If operated at a current density of 0.5 A/cm², this SOM electrolyzer would be capable of producing ~1.3 kg/day of magnesium. This SOM electrolyzer was operated at 7 V and 205 A to generate magnesium at a rate 2.2 kg/day. Unfortunately the electrolysis had to be stopped after couple of hours. The long stainless crucible-condenser assembly expands much more than the furnace or its tube during heating from room temperature to 1150-1200°C, and our attempts to accommodate this expansion led to crucible weld failures. The leakage of molten salt and magnesium through the failed weld joints led to breakage of the quartz furnace tube. For this reason we could not collect any magnesium in the condenser. During the electrolysis the anode current collector also failed. The large amounts of oxygen generated at the anode due to the high current led to the oxidation of the nichrome current collector and the oxide scale on the nichrome alloy was not durable.

Based on these results, we fabricated a current collector (described in Figure 3: right) and built a single-tube SOM with a shallow immersion (1" immersion depth) to test durability of the LSM/nichrome current collector. We operated the SOM electrolyzer for more than 80 hours. Figure 12 shows the current during the electrolysis run. The current was low in comparison to previous experiments, due to the use of a high-resistance current collector. The current density was around 0.15 A/cm² at 5.0 V. The voltage drop was due to high contact resistance at the junction between the 3 cm LSM rod and the thin nichrome wire. Though its resistance is high, this type of current collector has had

the best long-duration performance. There was no fluctuation in current for nearly 80 hours.

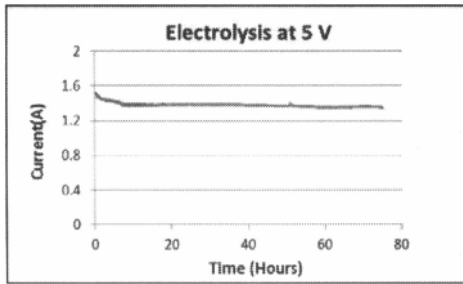


Figure 12. Current-time scan during the electrolysis.

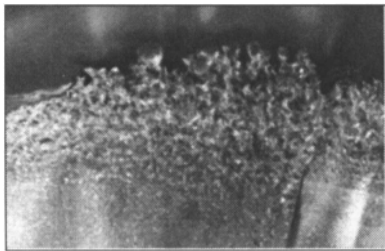


Figure 13: Metal deposit on stainless shim from the 80-hr experiment

Figure 13 shows the metal deposit on the stainless steel shim after the electrolysis. This shows that LSM/nichrome might be good candidate for a current collector if the contact resistance can be lowered. To lower contact resistance we intend fabricate a multi-component current collector current collector shown in Figure 14.

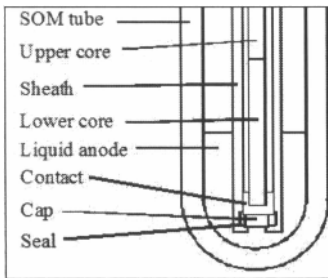


Figure 14. Current collector design which mechanically constrains the cap.

It shows schematically the components of our current collector approach, with material properties as follows:

Upper core: very high electrical conductivity, particularly electronic conductivity.

Lower core: very high electrical conductivity, melting point above operating temperature, and low solubility in the contact material.

Contact: solidus point below operating temperature, and good electrical conductivity in the liquid or semi-solid state at operating temperature.

Seal: liquidus point and/or glass transition above operating temperature, minimal solubility in the liquid metal anode, stability in liquid metal anode supersaturated with oxygen, low oxygen diffusivity, ability to provide a hermetic seal between two solids at operating temperature optionally by creep and/or glass flow, but with high enough viscosity or low enough creep rate to not flow out of the cap-sheath gap.

Sheath: stability in pure oxygen at operating temperature and between operating and ambient temperatures, low thermal conductivity, and resistance to failure due to temperature gradients or thermal or mechanical shock which would allow oxygen breach.

Cap: at operating temperature, minimal solubility in the liquid metal anode, stability in pure oxygen, high electrical conductivity particularly electronic conductivity, and low oxygen diffusivity, implying low oxide ion conductivity. For this application, minimal oxygen diffusivity and minimal porosity are essential, making strontium-doped lanthanum manganite (LSM, La_{0.8}Sr_{0.2}MnO₃) a good candidate.

To accommodate the thermal expansion of the electrolyzer and to enable further scaling we have built a three-tube SOM electrolyzer with a new configuration, as shown in Figure 15. In this configuration the salt bath container and the condenser are side-by-side instead of top and bottom. This whole assembly goes in an inert enclosure containing separate heating elements for the salt bath container and the condenser. There are two advantages in this type of configuration. First, the smaller overall dimensions lead to less of a problem with thermal expansion making the weld joints more reliable. Second, there is a better control of the condenser temperature, which is vital for making liquid magnesium.

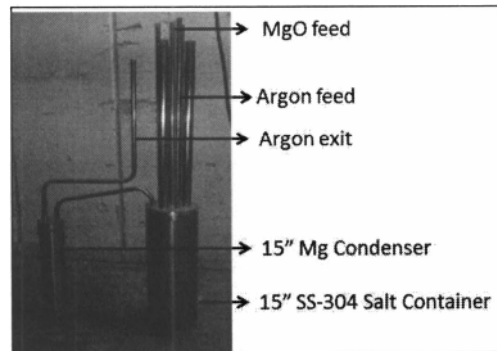


Figure 15: New side-by-side furnace design

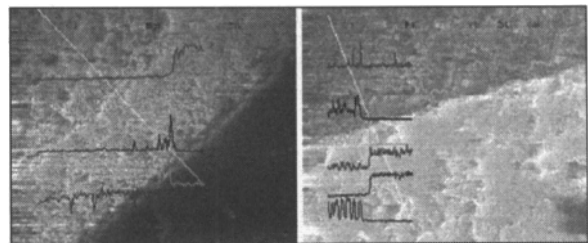


Figure 16. Microstructures for zirconia membranes after electrolysis, with EDAX line scans overlaid. Left: no added YF₃, right 3.39 wt% YF₃.

After all the experiments we performed micro structural analysis of the zirconia tubes. Figure 16 shows the microstructure of the SOM exposed to molten fluoride salt without YF_3 (left) and with YF_3 (right) under electrolysis conditions. It clearly shows that YSZ exposed to molten salt that does not contain YF_3 develops a yttria-depleted zone near the exposed surface, while YSZ exposed to molten salt with YF_3 shows no such degradation. Krishnan (5) observed a similar phenomenon and showed that adding YF_3 to the flux inhibits formation of a yttria-depleted layer. Therefore, adding YF_3 to the molten salt inhibits yttrium leaching, thus increasing the durability of zirconia tubes.

To further analyze the SOM degradation mechanism of the zirconia tubes, we performed static exposure experiments, which exposed the SOM to molten salt at standard operating temperature with no current. Figure 17 shows a comparison of the yttrium composition at SOM/molten salt interface. It can be clearly seen that the composition profile changes in zirconia in static contact with molten flux are nearly identical to those following an electrolysis experiment. This indicated that the primary mechanism of degradation is not related to the passage of ionic current through zirconia.

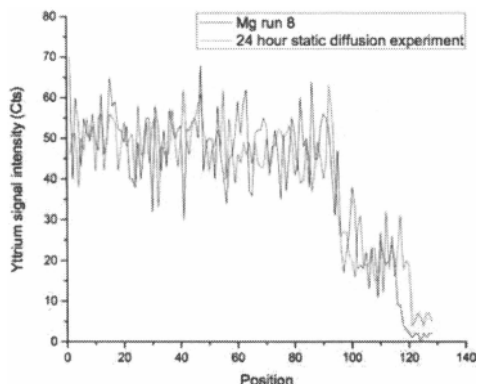


Figure 17: EDAX yttrium line scans from samples immersed in molten salt for 24 h with no added YF_3 . Red – immersion only. Black – after electrolysis.

Based on these results, we concluded that membrane degradation is primarily due to dissolution of yttria in the flux and the passage of electronic current through the zirconia tubes. Therefore, inexpensive static exposure experiments can provide the information necessary to assess the former corrosion mechanism of the zirconia tubes.

Towards that end, Figure 18 shows the comparison of as-received zirconia tube from the vendor and the zirconia tube after exposure to flux for different durations. The membranes exposed to flux for 100 hours and 500 hours show some degradation, but SOM exposed for 32 hrs shows little to no degradation under static or electrolysis conditions.

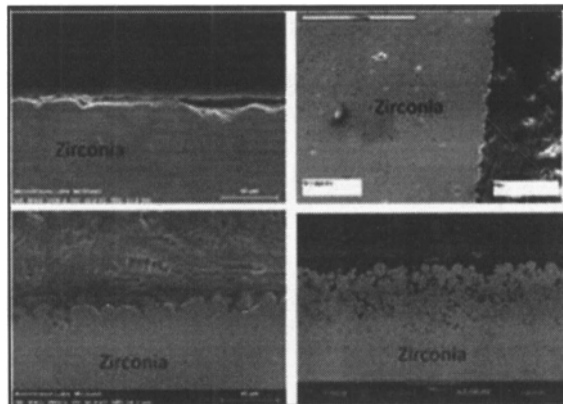


Figure 18. SEM micrograph of the SOM-flux interface: as-received (top-left), 32-hour exposure (top-right), and 100 hour exposure (bottom-left), 500-hour exposure (bottom-right).

Summary

The SOM electrolysis process produces high-purity magnesium efficiently from available industrial-grade magnesium oxide with zero emissions and with a salable pure oxygen by-product, creating a low-cost magnesium product to facilitate its use in light-weight vehicles. The zirconia solid electrolyte between the molten salt and inert anode protects the anode, blocks oxygen back-reaction with magnesium, and makes the oxygen by-product very pure. The design where the LSM is attached to nichrome can be a durable current collector if the contact resistance is lowered. The temperature of the condenser has to be carefully controlled to generate liquid magnesium. Finally, the zirconia tube durability can be increased by controlling the composition and the microstructure carefully.

Acknowledgements

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