

EFFICIENCY AND STABILITY OF SOLID OXIDE MEMBRANE ELECTROLYZERS FOR MAGNESIUM PRODUCTION

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Abstract

Solid oxide membrane (SOM) process has been successfully employed for the production of magnesium directly from its oxide. The process involves dissolving MgO in a fluoride based ionic flux and electrochemically pumping out the oxygen ions from the flux via an oxygen-ion-conducting SOM to the anode where they are oxidized, while reducing magnesium ions at the cathode. Understanding the long-term stability of the SOM in the flux is critical for the commercial success of this technology. In this study long term SOM stability is investigated under potentiostatic conditions. Additionally, study utilizes electrochemical techniques such as impedance spectroscopy and linear sweep voltammetry to investigate key concepts related to MgO dissociation and current efficiency. Results show that the dissociation potential of MgO is dependent on the partial pressures at which magnesium is generated and the membrane stability is likely related to the current efficiency.

Introduction

Magnesium is a leading candidate material to replace steel and aluminum in automobiles for reducing vehicle weight to increase fuel efficiency. Since magnesium is 36% lighter per unit volume than aluminum and 78% lighter than steel estimates show that 22.5 kg of mass reduction would improve fuel efficiency by around 1% [1]. Currently world magnesium production is around 400,000 tonnes per annum and demand for magnesium is expected to grow by 7% per annum [2]. To meet this future demand for primary magnesium, the current technologies have to be made more efficient and new technologies must be explored.

One promising new technology is the solid oxide membrane (SOM) electrolyzer that has the potential to produce primary magnesium at a fraction of its current cost with the added benefit of being environmentally friendly [3, 4]. However, one challenge for the SOM electrolyzer is the long term stability of SOM in a magnesium oxide containing molten flux at high temperatures (1100-1200°C). Previous studies show that fluoride based ionic flux is suitable for the SOM electrolysis [3]. However, long term stability of SOM in the molten flux for more than 2000 hrs is needed before the SOM electrolyzer can be commercially used for magnesium production.

We believe the SOM can degrade in two possible ways: 1) Leaching of yttria from the SOM into the molten flux, and 2) Electronic current in the cell. Some initial studies show that leaching of yttria from the SOM into the molten flux can be prevented by adding yttrium fluoride in the flux to balance the activity of yttrium in the membrane and yttrium in the flux [5].

The second pathway for SOM degradation is due to electronic current in the system, and this is evaluated in this article. Suput et al. [6] employed the SOM electrolyzer to produce titanium and showed that the multi-valence state of Ti in the flux resulted in electronic current in the SOM process. The electronic current degraded the SOM and the efficiency was significantly lower. In that study it was also reported that by using an electron blocker, the degradation of the SOM decreased significantly and increased the overall efficiency of the SOM electrolyzer.

The advantage of the SOM electrolyzer for magnesium production is that the magnesium is not multivalent as titanium. Therefore, the flux is essentially ionic and acts as an electron blocker. However, Krishnan et al. [5] observed a small current prior to the dissociation potential of MgO during the potentiodynamic scan and attributed that to the oxygen impurities in the cell. This so-called "leakage current" was also reported in the SOM process for calcium production and it increased with electrolysis time [7]. The increase in leakage current was attributed to electronic current resulting from solubility of metallic calcium in the fluoride based flux [8]. As mentioned before, when the flux becomes electronic the efficiency decreases and also leads to degradation of the membrane. Therefore it is critical to study the nature of the current in the SOM electrolyzer. In this paper we characterize the SOM electrolyzer electrochemically to understand the origins of the leakage current. This is very essential to formulate strategies for reducing or eliminating leakage current and thereby increase process efficiency.

Experimental

Experimental set-up: Figure 1 shows the design of SOM electrolyzer used in the present experiments. It consists of an upper electrolysis chamber, heated to 1200°C and a lower condensation chamber kept at a temperature range of 1150°C-500°C. The set-up is fabricated using SS-304 (Grade 304 stainless steel) and heated as mentioned above in a reducing atmosphere (5% H₂-Ar). The electrolysis chamber contains a 0.75" outer diameter yttria stabilized zirconia tube (McDaniel Ceramics) immersed in a molten flux (55 % MgF₂-45%CaF₂-10% MgO). The stainless steel crucible wall of the electrolysis chamber served as the cathode and silver inside the YSZ tube served as the anode. An alumina spacer was used to insulate the YSZ membrane from the steel which acted as the cathode. A ¼" molybdenum tube (Nanmac) served as the anodic current collector. When the electric potential applied across the cathode and the anode exceeded the dissociation potential of magnesium oxide, magnesium vapor is produced on the stainless steel cathode. It should be noted that during electrolysis the cathodic chamber of the cell is purged with Ultra High Purity Argon (Airgas) at

300cc/min through the annulus between a 1 ¼" inner diameter SS-304 tube and 0.75" outer diameter YSZ tube to lower the partial pressure of magnesium vapor that is produced over the cathode. This is done in order to prevent the reduction of YSZ with magnesium vapor. The magnesium vapor produced on the cathodic side is transported to the condensation chamber by two ¼" outer diameter and 0.12" inside diameter SS-304 tubes. The inlets of these two tubes extend above the flux to prevent any molten flux from entering the condenser. On the anodic side, hydrogen was bubbled in the silver through the molybdenum tube at rate of 60cc/min prevent the molybdenum current collector from oxidizing. Part of the hydrogen also acts as a reductant and the overall cell reaction is given as:

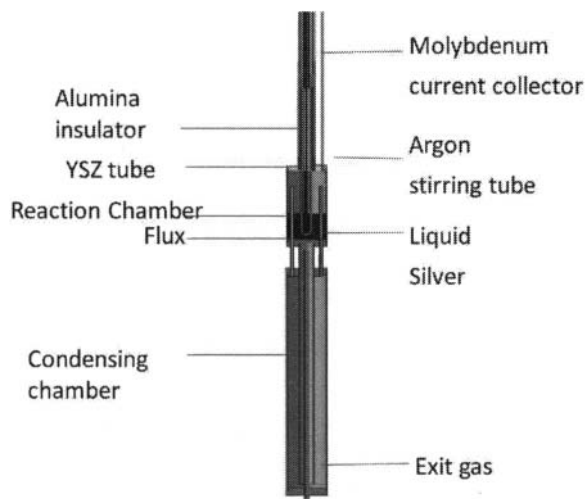
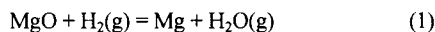


Figure 1. Design of experimental setup for SOM process.

All electrochemical measurements were performed using a Princeton Applied Research Potentiostat model 263A and a Solartron Frequency Response analyzer model 1250. Electrolysis of magnesium was carried out using an Agilent Technologies N5743A Power Supply.

Results and Discussion

Electrochemical measurements: When the SOM electrolyzer was at the desired temperature, pre-electrolysis was performed at an applied potential less than the dissociation potential of magnesium oxide to remove any dissolved oxygen in the flux. Previous studies report that the dissociation potential of MgO in a SOM electrolyzer with hydrogen at the anode is around 0.7 V [3]. Therefore, pre-electrolysis was performed at a potential 0.5 V. Figure 2 shows that after 15 minutes, the current drops to around 0.01 A, which suggests that most of the dissolved oxygen in the flux has been removed. The initial current is most likely due to a small amount of oxygen that is not removed during the purging process.

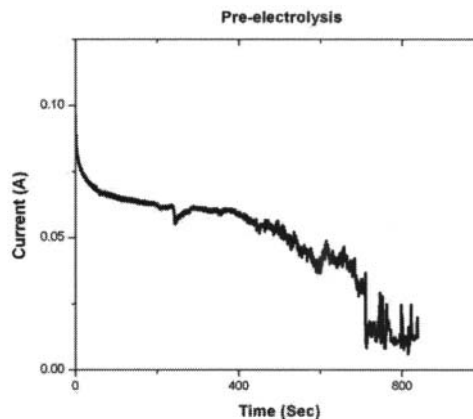


Figure 2. Pre-Electrolysis potentiostatic hold at 0.5V

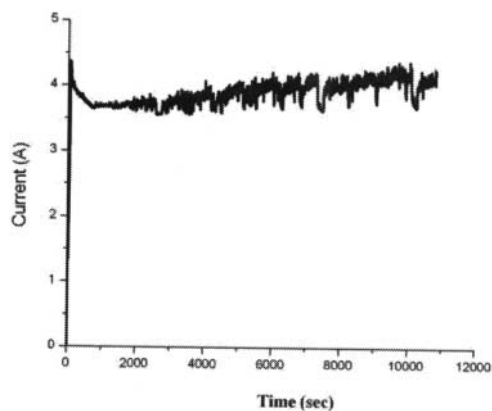


Figure 3. Current-voltage characteristics during electrolysis at 2.6V

Figure 3 shows the current-time characteristics when electrolysis was performed at 2.6 V. It shows initially that the current dropped from 4.4 A to 3.7 A during the first 1000 seconds. Then the current increased slowly and was around 4.0 A after 11000 seconds of electrolysis. This is not expected because with increase in duration of electrolysis the amount MgO in the flux decreases and therefore the mass transfer resistance of oxygen ions in the flux is expected to increase and the current should decrease. Potentiodynamic scans performed before and after electrolysis further show that during electrolysis the contribution of leakage current increases (Figure 4). The possible reason for this could either be a leak of H₂O from the anodic side or electronic current due to dissolution into the flux of metallic magnesium and/or calcium produced during electrolysis.

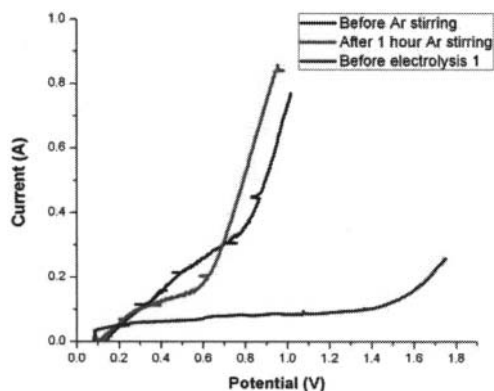


Figure 4. The effect of argon stirring on the leakage current

1) H₂O leak from anodic side: It has been shown previously that even a P_{O₂} of 10⁻¹⁴ atm will lead to noticeable leakage current [5]. In that study the SOM electrolyzer experiments relied on a metal to ceramic seal at a high temperatures. In this study the design was changed so that all of the ceramic- metal sealing was moved to the room temperature region on the top of the set-up using Swagelok UltraTorr fittings. This significantly reduces the potential for H₂O leak from the anodic side and therefore also the leakage current. Although leakage current of this nature decreases the efficiency, it is not expected to degrade the membrane.

2) Metal Solubility: Another potential reason for the leakage current is the dissolution of metallic magnesium and/or calcium in the flux. It is widely known that calcium has a very high solubility in calcium halides [8]. Dissolution of metals in the flux which is originally ionic in nature can cause the flux to start conducting electronically. This can be very detrimental to the SOM electrolyzer as it could potentially reduce the zirconia in the membrane and ultimately degrade the membrane, reducing its lifespan.

It has been shown that magnesium metal does have some solubility in chloride based ionic salts [9]. In that study metallic magnesium and magnesium chloride were melted together and samples from the melt were cooled to room temperature. These samples were then dissolved in dilute acid to produce hydrogen. From the amount of hydrogen evolved the amount of dissolved magnesium was calculated.

In order to determine whether there is any dissolved metal in this flux after electrolysis, dilute acid was added to the flux in a closed container and the increase in pressure due to the formation of hydrogen gas measured. The dissolved metal, Mg and/or Ca in the flux after electrolysis, was estimated to be between 0.02-0.05% by weight. For comparison, a similar procedure was performed on the fluoride flux prior to electrolysis and no hydrogen evolution was detected indicating that prior to electrolysis the flux did not have any metal in solution.

Although the presence of soluble metal in the flux was detected after electrolysis it could not be determined whether the metal was magnesium or calcium. Since the flux contains both calcium and magnesium ions along with oxygen ions, there exist finite activities of both CaO and MgO in the flux. Therefore the metal in solution could be either Mg or Ca or both.

It is possible to lower the activity of the dissolved metal in the flux by stirring the flux with an inert gas such as argon. Figure 4 compares the potentiodynamic scans with and without argon stirring in the flux. This shows that the leakage current can be lowered by stirring argon for an hour but it could not be eliminated.

Although stirring argon did not eliminate the leakage current, it did decrease the dissociation potential of magnesium oxide which in turn decreases the energy requirements of the SOM process. The dissociation potential decreased from 1.4 volts without argon stirring to 0.7 V [Figure 5] with it. The reason for decrease in the the dissociation potential is because magnesium evolves at a lower partial pressure when argon is stirred during electrolysis. The Nernst equation for reaction 1 is given by equation 2.

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{MgO(l)} \cdot P_{H_2(g)}}{P_{Mg(g)} \cdot P_{H_2O(g)}} \quad (2)$$

Since E⁰ is negative, |E| decreases when P_{Mg(g)} decreases. It is believed that the P_{Ar(g)} coming out of the stirring tube is very near 1 atm and therefore P_{Mg(g)} must be very low. Since the stirring tube also acts as a cathode it provides a location for magnesium oxide reduction at a lower potential.

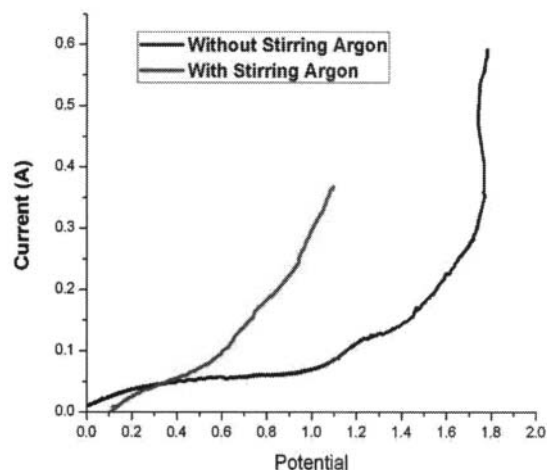


Figure 5. Comparison of potentiodynamic scans with and without argon showing change in dissociation potential

Conclusion

The SOM process is a method for producing magnesium directly from its oxide. The current increased during electrolysis and this was primarily attributed to dissolution of magnesium and/or calcium in the flux that is produced during electrolysis. The leakage current not only lowers the efficiency but also accelerates the degradation of SOM. The leakage current was lowered by stirring argon in the flux. The dissociation potential depends on the partial pressure at which the magnesium is produced, and also decreased with stirring argon in the flux.

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