

Electrowinning Magnesium Metal from $\text{MgCl}_2\text{-NdOCl}$ Melt Using Solid-Oxide Oxygen-Ion-Conducting Membrane Technology

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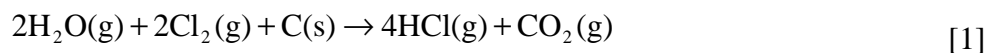
Abstract:

A new electrolytic process for extraction of magnesium metal from its oxide is demonstrated. It is based on the chemical system $\text{MgCl}_2\text{-NdCl}_3\text{-MgO}$. It has been shown previously that NdCl_3 and MgO react to form NdOCl , and this study has employed a $\text{MgCl}_2\text{-NdOCl}$ melt in order to focus attention on the electrolytic, metal-making process itself. Two main experiments are discussed here. In the first, liquid magnesium metal is produced from a $\text{MgCl}_2\text{-NdOCl}$ melt at 700°C with a graphite cathode and graphite anode. In the second, liquid magnesium metal is produced from the same melt at 690°C with a graphite cathode and porous nickel-yttria-stabilized-zirconia cermet anode. In this second electrolytic cell, the anode is separated from the liquid electrolyte by an oxygen-ion-conducting, yttria-stabilized zirconia ceramic membrane, which should ensure that water vapor is produced at the anode, rather than CO , CO_2 , or Cl_2 . Magnesium metal globules are observed in the frozen melt in the vicinity of the cathode after completion of each experiment, and the metal composition is determined using electron probe microanalysis.

I. Introduction

A. Current Processes Used to Produce Primary Magnesium Metal

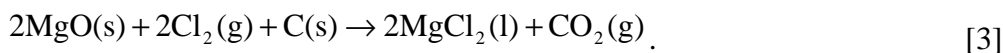
Magnesium is produced commercially by two methods: electrolytic and metallothermic. One electrolytic method uses a $\text{MgCl}_2\text{-NaCl-KCl-CaCl}_2\text{-CaF}_2$ melt at 750°C . The MgCl_2 is electrolyzed to produce magnesium metal at the cathode and Cl_2 gas at the anode (Figure 1). The cathode is steel and the anode is carbon. The metal floats to the surface, since the density of the liquid metal is less than that of the molten chloride electrolyte; a ceramic separator prevents contact between the liquid metal and the anode gases. Periodically magnesium metal is removed from the cell, and MgCl_2 feedstock is added. The electrolytic method has the disadvantage that either the MgCl_2 feed must be dehydrated completely, or a consumable carbon anode must be employed. These alternatives are not economically or environmentally attractive. If the MgCl_2 feedstock contains residual water, then the carbon anode is consumed,



or MgO is produced,



The MgO has very low solubility in the chloride electrolyte and either sinks to the bottom of the cell, forming a sludge that traps magnesium metal globules, or reacts at the carbon anode with $\text{Cl}_2(\text{g})$,



In the metallothermic method, burned dolomite, ferrosilicon, and fluorspar are mixed, placed in an externally heated steel retort, and heated to 1200°C . A reduced pressure of 0.1 kPa is used. Magnesium vapor is produced, and this condenses in the cool end of the retort. The shortcomings of the metallothermic route are that it is a batch process, the ferrosilicon is expensive, and the reactor is difficult to scale-up.

B. Electrolytic Production of Magnesium Metal from Impure MgCl_2 or MgO Feedstocks

The electrolytic process is favored in the primary magnesium production industry. It is continuous and can be scaled up. As mentioned previously, the conventional electrolytic process uses MgCl_2 feedstock. The preparation (purification and drying) of this feed material is expensive, accounting for a large fraction of the total production cost of magnesium metal. There has long been interest in producing magnesium metal from magnesium oxide (MgO) or impure MgCl_2 feedstock by a continuous electrolytic process. Use of MgO is attractive in many areas, especially those with large reserves of magnesite or dolomite. Magnesium oxide is currently produced commercially from dolomitic limestone ($\text{CaCO}_3\cdot\text{MgCO}_3$), natural magnesite (MgCO_3), seawater, and brine by a number of different processes.^[1]

In 1941, the U.S. Bureau of Mines initiated a program to develop a new process for magnesium production from dolomite and low-grade magnesite.^[2] Two years of development followed, and it was concluded that magnesium metal could be produced from MgO in a fused MgCl₂ bath. However, a sludge of MgO, magnesium metal, and other species collected in the cell, and this had to be periodically removed to prevent short-circuiting. These researchers postulated that electrolysis of MgCl₂ locally produced Cl₂ at the anode, and that this gas reacted with carbon and undissolved MgO in the vicinity of the anode to produce CO₂ (Eq. [3]). The compound MgO was considered an anode “depolarizer” and sufficient MgO was added to suppress most Cl₂ evolution from the cell. Although these researchers were able to produce magnesium continuously, their approach was not adopted.

Several U.S. patents have recently been assigned to General Motors (Detroit, MI) for processes and electrolyte compositions (Table 1).^[3-8] These patents offer a number of ideas relating to use of MgO for magnesium metal production. One idea is to use a molten electrolyte containing rare earth (RE) chlorides, as well as the traditional alkali metal and alkaline earth chlorides. When MgO is added to the electrolyte, a chemical reaction between MgO and the RE chloride occurs; this reaction produces chlorides and oxychlorides that dissolve in the electrolyte. A second similar idea involves use of a molten electrolyte containing RE fluorides and other group 1 and group 2 metal fluorides. In this case, when MgO is added to the electrolyte, a chemical reaction between MgO and the RE fluoride occurs, which produces soluble fluorides and oxyfluorides. A third idea is to use a mixture of inexpensive fluorides and chlorides as the electrolyte. When MgO is added to this mixed chloride-fluoride electrolyte, a series of reactions, some chemical and some electrochemical, occurs, and magnesium metal is produced (Table 2). Some test data is provided in these patents, and a description of the RE-chloride-based process is available in the literature elsewhere,^[9] but it is unclear in some cases whether the ideas in the patents have been fully tested, or are mostly the result of theoretical calculations.

Cathro, Deutscher, and Sharma tried to produce magnesium metal directly from MgO in a chloride-based electrolyte containing the RE chloride NdCl₃.^[10] They used a liquid tin cathode and a carbon anode, and they produced a Sn-Nd-Mg alloy. The magnesium content of the alloy was very low (approximately 0.5 wt%), and a large amount of high-Nd-content metal fines were generated in the electrolyte. The anode gas was mainly Cl₂, rather than CO₂ or CO.

C. Goals of Present Investigation

In this study, the investigators sought to produce magnesium metal directly from MgO by an electrolytic process. The first goal was to demonstrate that this could be done with an electrolyte similar to that employed by Cathro et al.^[10] A solid graphite cathode was used instead of molten tin, and the anode was also graphite. The second goal of the study was to electrolytically produce the metal again, using the same electrolyte, but in a cell with different anode. In this case, the cathode was graphite, and the anode was a porous nickel-yttria-stabilized-zirconia cermet coating applied on one side of an oxygen-ion-conducting, yttria-stabilized zirconia ceramic membrane. The membrane separated the anode from the molten electrolyte. The present investigators were interested in demonstrating that solid oxygen-ion-conducting membrane (SOM) technology can be applied to electrolytic magnesium production. Possible benefits of SOM in this case include the following: the anode is non-consumable; the product gas is H₂O rather than CO, CO₂, or Cl₂; and so long as the oxygen-ion-conducting membrane is stable, relatively high electric potentials can be applied to the cell without causing dissociation of the molten chloride electrolyte.

II. Experimental

A. Preparation of batch powder

In the MgCl_2 - NdCl_3 - MgO system, MgO reacts with NdCl_3 to form NdOCl , which is then dissolved by MgCl_2 - NdCl_3 ,



This reaction in Eq. [4] was shown to occur when a mixture of MgO , MgCl_2 , and NdCl_3 is held at 760-790°C for 1-2 h.^[10] The solubility of NdOCl in MgCl_2 is approximately 40 mol% (58 wt% NdOCl) in the range 700-800°C.^[11] The solubility of NdOCl in NdCl_3 is approximately 17 mol% (14 wt% NdOCl) in the same temperature range.^[12] The product NdOCl of the reaction in Eq. [4] is therefore expected to dissolve in MgCl_2 and NdCl_3 .

In this study, a batch composition of 80 wt% MgCl_2 -20 wt% NdOCl was used. When NdOCl is used instead of MgO in the batch, there is no need during the experiment to wait for the reaction in Eq. [4] to take place; one can immediately begin electrolysis once fusion of the batch is complete. In some preliminary experiments, a batch composition of 50 wt% MgCl_2 -50 wt% NdOCl was used; this is close to the eutectic composition in the MgCl_2 - NdOCl system according to one study.^[11] Several observations indicated that the melt based on a 50% MgCl_2 -50% NdOCl batch is not completely molten, or has a very high viscosity. For example, at the end of one experiment using 50 wt% MgCl_2 -50 wt% NdOCl , the YSZ tube was raised out of the melt at 900°C, and after waiting 30 minutes at 900°C, the melt was cooled at 3°C min⁻¹ to room temperature. Examination of the crucible showed a deep pit in the frozen melt; the melt did not flow after removing the tube.

The MgCl_2 used in the batch is prepared by heating commercial anhydrous MgCl_2 under flowing HCl gas to eliminate residual moisture in the as-received MgCl_2 .^[13] The NdOCl is prepared by heating commercial $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ under flowing air.^[14] Both the MgCl_2 and NdOCl preparation procedures used in this study were validated by x-ray diffraction (XRD) tests on the products: no peaks for MgO or hydrated magnesium chloride are observed in the scan on MgCl_2 , and no peaks for Nd_2O_3 or neodymium chloride are observed in the scan on NdOCl . The batch for each experiment comprised 84 g NdOCl and 320 g MgCl_2 , both prepared beforehand and stored before use in a glove box. The batch ingredients were weighed into a plastic milling bottle, and then mechanically mixed by rolling on a ball mill without milling media for over one hour just prior to the experiment.

B. Electrolytic Cell with Graphite Anode and Graphite Cathode

Two different types of experiment were conducted. In the first, a solid graphite cathode and solid graphite anode were used (Figure 2). This experiment was conducted to test the hypothesis that magnesium can be produced at unit activity by electrolysis of a MgCl_2 - NdOCl melt. The anode was a graphite crucible (inner diameter 64.3 mm, inner depth 121.6). The cathode was a graphite rod (outer diameter 13.5 mm, length 100 mm). Eight grooves were machined in this rod to trap magnesium metal globules.

An MgO crucible (outer diameter 51.4 mm, inner diameter 45.0 mm, inner depth 82.9 mm) with six pre-cut horizontal slits was placed in the bottom of the graphite crucible (anode).

The graphite cathode rod was placed vertically in the MgO crucible, and the batch powder was added to both the MgO and the graphite crucible (341.017 g total). The depth of the batch was 100 mm. A graphite crucible cover was placed on the graphite crucible, and an alumina tube (outside diameter 13 mm, inside diameter 10.5 mm) was placed in a hole machined in the center of the cover, so that the tube rested on the top of the graphite rod. The graphite crucible was raised into a vertical tube furnace on a steel platform, which was a steel disc threaded on a 12.7-mm steel rod. This steel rod was the anode rod, connected by a wire to the positive pole on the DC power supply (Hewlett Packard model 6033A) used during the experiment. The furnace tube was mullite, lined with graphite foil to prevent attack by the furnace gases, especially the gas HCl that formed during heating through the temperature range 200-300°C. It seems likely that the HCl formed as a result of the reaction between residual water in the feed with MgCl_2 (see Eq. [2]). Seven layers of alumina-silica thermal insulation were placed beneath the crucible platform. A type K (chromel-alumel) thermocouple was placed 1 to 2 mm from the underside of the crucible platform to monitor the experiment temperature. A 6.35-mm steel rod was lowered from the top end of the furnace tube, and threaded into the upper end of the graphite cathode rod. This steel rod was the cathode rod, and was connected by a wire to the negative pole on the DC power supply. Two layer of insulation were placed over the crucible cover, and then three alumina crucibles filled with titanium metal sponge were placed on the insulation. Five more layers of insulation were placed over the titanium-filled crucibles. The furnace was sealed, and 750 mL(STP) min^{-1} of 98 vol% Ar-2 vol% H_2 gas was passed through the system. The gas entered at the bottom of the furnace tube, and exited at the top. The furnace was heated at 3°C min^{-1} to 700°C. After waiting approximately 1 hour at 700°C to allow for fusion and homogenization of the molten electrolyte, the DC power supply was used to pass current through the cell in constant current mode. After the experiment was complete, the furnace was cooled at 3°C min^{-1} to room temperature.

C. Electrolytic Cell with Ni-YSZ Cermet Anode and Graphite Cathode

In the second type of experiment, a solid graphite cathode was used, and the anode was a porous ceramic-metal (cermet) layer, consisting of nickel metal and Y_2O_3 -stabilized ZrO_2 (YSZ). The layer was deposited on the inside of a bottom-end-closed YSZ tube, and this tube was dipped into the melt (Figure 3). This experiment was conducted to test the hypothesis that magnesium can be produced at unit activity on a graphite cathode by electrolysis of a MgCl_2 - NdOCl melt in a cell with a Ni-YSZ cermet anode separated from the melt by a YSZ membrane. The construction of the cell is different than in the previous experiment, but the experimental procedure is similar.

To form the anode the following procedure was used. A bottom-end-closed YSZ tube (outside diameter 12.69 mm, inside diameter 9.83 mm, overall length 204 mm) was washed with water, rinsed with methanol, and dried at 50°C to constant weight. The YSZ tube was removed from the drying oven and allowed to cool to room temperature. A batch of 10 g YSZ powder (Tosoh TZ-8Y) and 30 g NiO (J.T. Baker) powder was wet-milled in methanol with YSZ milling beads for four hours. This slurry was dried at 50°C for 24 hours, and then the milling beads were separated from the powder using a coarse sieve. The dry YSZ-NiO powder was passed through a 270-mesh screen. A 10 mL graduated cylinder was filled with 2 mL methanol and 4.2 g of YSZ-NiO powder, and the mixture was stirred using an ultrasonic cleaning machine. Approximately 3 cm^3 of slurry was produced. The slurry was poured into the YSZ tube, and the tube was shaken to apply the slurry evenly on the inside walls of the tube. The YSZ tube was

immediately placed upright in a vacuum chamber, and the pressure was reduced to approximately 1 mm Hg (0.1 kPa) to remove most of the methanol from the coating. The coating added 1.8-1.9 g to the weight of the YSZ tube. The green coating was dried in air at room temperature for 3 to 4 days, and then placed in a vertical tube furnace.

Compressed air was passed ($520 \text{ mL (STP) min}^{-1}$) into the YSZ tube using a 6.35 mm-outside diameter alumina tube; the alumina tube was placed inside the upper end of the YSZ tube approximately 2 cm. The YSZ tube was heated at 3°C min^{-1} to 1500°C . After holding at 1500°C for five hours in flowing air to sinter the YSZ-NiO coating, the furnace was cooled at 3°C min^{-1} to 1200°C . The alumina gas tube was then lowered inside the YSZ tube to within 2 cm of the bottom (closed) end, and the gas was changed from compressed air to Ar (99%). After 30 minutes of Ar flow at 1200°C , the gas was changed to N_2 -5 vol% H_2 . After one hour at 1200°C to reduce NiO to Ni, the furnace was cooled at 3°C min^{-1} under flowing N_2 -5% H_2 to room temperature. The YSZ tube was removed, and the resistance of the cermet coating was measured using two copper-wire probes and a multimeter. This anode is similar to that used in solid oxide fuel cells.^[15]

To fabricate the anode assembly, an alumina extension tube was glued to the open end of the YSZ tube; a boron nitride coupling was machined to fit inside both tubes, and a ceramic glue was applied to make a gas-tight joint. A 6.35 mm-diameter stainless steel tube with nickel metal gauze welded to its outside surface over the lower 18 cm was inserted into the YSZ-and-alumina tube. The nickel gauze allows for electrical contact between the stainless steel tube and the cermet coating without obstructing gas flow. During the experiment, N_2 -5 vol% H_2 would flow downward in the gap between the YSZ tube and stainless steel tube, and upward inside the stainless steel tube.

The cathode was a graphite rod (outside diameter 13 mm, length 127 mm); as in the previous experiment, this rod was tapped to receive a 6.35 cm-diameter steel rod to make electrical contact. To separate the catholyte from the bulk electrolyte, an MgO tube (22 mm outside diameter, 17 mm inner diameter, 152 mm length) was placed coaxially with the graphite cathode rod. The MgO tube was held in place by a graphite plug that rested on the top of the graphite cathode rod. Two square-shaped areas were removed from the lower end of the MgO tube to provide contact between the catholyte with the bulk electrolyte. Since the cathode was separated from the gas atmosphere by the MgO tube and graphite plug, no crucible cover was used.

A MgO disc was placed in the bottom of the graphite crucible (63.6 mm inner diameter, 152 mm inner depth). The graphite cathode rod, graphite plug, and MgO separator tube were placed in the crucible; the end of the MgO tube and graphite rod were flush and both resting on the MgO disc. Batch was added to the crucible (377.044 g total). The graphite crucible was raised into the furnace tube, thermocouple raised to the underside of the crucible platform, and insulation placed beneath the crucible, as in the previous experiment. A 6.35 mm-diameter steel rod was lowered from above through an opening in the graphite plug, and threaded into the graphite cathode rod. The anode assembly was lowered until it rested on the top of the batch powder.

Four layers of silica-alumina insulation were lowered over the graphite crucible, and then the titanium sponge was placed, as in the previous experiment. Six more layers of insulation were placed above the titanium. The furnace tube was sealed and Ar (99% pure) gas was passed (flow rate $2100 \text{ mL (STP) min}^{-1}$). The gas entered the bottom of the furnace tube, and exited at the top. A second gas stream of 95 vol% N_2 -5 vol% H_2 at $660 \text{ mL (STP) min}^{-1}$ entered at the top

of the anode assembly, passed downward in the space between the ceramic tubes (YSZ and Al_2O_3) and the stainless steel tube, and returned upward inside the stainless steel tube to the exit at the top of the anode assembly. A high gas flow rate was used to avoid concentration polarization at gas-cermet interface. The furnace was heated at $2.5^\circ\text{C min}^{-1}$ to 690°C . After waiting approximately two hours at 690°C to allow for fusion and homogenization of the molten electrolyte, the DC power supply was used to pass current through the cell. The negative pole of the power supply was connected to the 6.35 mm-diameter steel rod, which was connected to the graphite cathode rod. The positive pole of the power supply was connected to the 6.35 mm-diameter stainless steel tube, which was connected to the Ni-YSZ cermet anode. Current was passed in constant-current mode. After the experiment was complete, the anode assembly was raised 76 mm, and the furnace was cooled at 3°C min^{-1} to room temperature.

III. Results

A. Experiment #1: Graphite anode and graphite cathode

The DC power supply was used in constant-current (galvanostatic) mode to pass current through the cell. The voltage was recorded continuously during the experiment. A summary of the current and voltage during the experiment is provided in Table 3. The total charge passed through the cell is approximately 16000 C (Figure 4). After the experimental apparatus returned to room temperature, it was disassembled. The titanium sponge, which initially weighed 24.172 g, gained 2.553 g. (This weight-gain is equivalent to 6 wt% conversion of Ti to TiO_2). Visual inspection revealed that the top 5 mm (total bed depth approximately 25 mm) was brown-black in color, whereas the initial color was metallic gray.

The total mass of the graphite crucible, MgO crucible, graphite cathode rod, and frozen electrolyte after the experiment was 757.77 g, whereas the initial mass of those items was 765.03 g. Cross-sectioning of the crucible revealed that the frozen melt depth was 68 mm. The batch weight was initially 341.017 g, and the available inner area in the graphite crucible (i.e. excluding MgO crucible and graphite rod) is 26.2 cm^2 , so the density of the frozen melt is approximately 1.9 g cm^{-3} . See Table 4 for anode- and cathode-melt areas, and current densities.

Metal globules were visible along the graphite cathode rod, over the bottom 2 cm of the rod (i.e. closest to the end that was resting on the bottom of the MgO crucible). The frozen electrolyte itself appeared to consist of two phases, one above the other, as if the melt separated into a low-density fraction and a high-density fraction. This observation had been made earlier in preliminary experiments, and x-ray diffraction analysis of each phase showed that the low-density phase was MgCl_2 -rich, whereas the high-density phase was NdOCl -rich. It seems likely that some NdOCl remained in solid form during the experiment, and that the lower portion of the melt was semi-solid, consisting of NdOCl solids suspended in MgCl_2 -rich liquid. The magnesium metal globules may have been held in place on the cathode rod by this semi-solid material. No magnesium metal globules were visible in the grooves that had been machined in the cathode rod; the grooved portion of the rod was exclusively in contact with the low-density, MgCl_2 -rich portion of the melt. The metal globules formed here may have floated to the top surface of the melt, and perhaps vaporized or reacted chemically with the gas phase.

The cathode was cut into pieces, and two were mounted in phenolic resin and carbon coated in preparation for electron probe microanalysis (EPMA) using a wavelength dispersive spectroscope (WDS). The standard used for magnesium was pure magnesium metal, and the

standard for neodymium was NdF₃. Several metal globules in each sample were analyzed. The analysis showed that the metal contained 99.0±0.2 wt% Mg and 0.33±0.18 wt% Nd; this is the raw data from WDS, and the total analysis for Mg+Nd is approximately 99.3 wt%. No inclusions were visible in the metal globules, although secondary electron imaging showed that two types of particles lay on the surface of the metal: one type was essentially MgCl₂, and the second was Nd-rich. Figure 5 is a back-scattered electron image of one metal globule.

B. Experiment #2: Ni-YSZ anode, YSZ membrane, and graphite cathode

A DC power supply was used to apply DC voltage to the cell (potentiostatic experiment). The investigators wanted to ensure that the applied potential did not exceed pre-determined limits (e.g. breakdown potential for MgCl₂, NdCl₃, or ZrO₂). The current was recorded continuously (Figure 6). The highest current was 0.19 A, and the current was 0.04 A for much of the experiment (steady-state). Figure 7 shows the charge passed through the cell as a function of time. The total charge passed was approximately 3350 C.

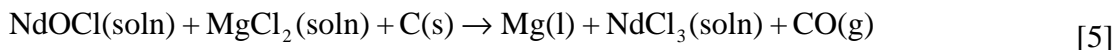
After the apparatus cooled to room temperature, the furnace was opened, the anode assembly and the graphite crucible were removed and inspected. A crater could be seen in the center of the frozen electrolyte, indicating that the melt did not flow after the anode assembly was raised at the end of the experiment. The thermocouple reading was 665°C when the anode assembly was raised, and fell at approximately 3.6°C min⁻¹ over the next twenty minutes (Table 5). In order to examine the interface between the cathode and the frozen melt, the bottom of the graphite crucible was cut off, and the MgO disc was removed. The open bottom of the graphite crucible, containing the frozen melt, MgO tube, and graphite cathode rod, was then ground on silicon carbide paper without any lubricant (Figure 8). Metal droplets were observed in the bulk electrolyte and in the catholyte (Figure 9). The frozen melt depth (excluding the MgO disc thickness) was approximately 68 mm. The batch weight was initially 377.044 g, and the available inner area in the graphite crucible (i.e. excluding MgO tube wall, YSZ tube area, and graphite rod) is 27.7 cm², so the density of the frozen melt is approximately 2.0 g cm⁻³. See Table 4 for anode- and cathode-melt areas, and current densities.

Two samples, consisting of metal globules and frozen melt, were mounted in phenolic resin and carbon coated for EPMA using WDS. The same standards were used as in the analysis for experiment #1. Several metal globules were examined, and both backscattered (Figure 10) and secondary electron (Figure 11) images were taken of one globule: these show that the metal is homogeneous, and small particles are visible on the metal surface, as in the analysis for experiment #1. The analysis showed that the metal contained 101.1±0.3 wt% Mg and 0.93±0.20 wt% Nd; this is the raw data from the WDS analysis, and the total analysis for Mg+Nd is approximately 102 wt%.

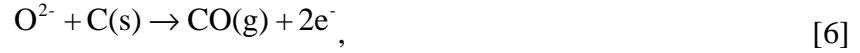
IV. Discussion

A. Experiment #1

Electrolysis of the melt should yield magnesium metal, according to the following overall reaction



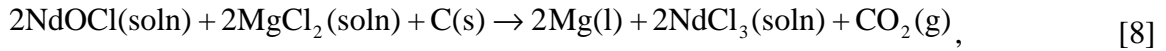
if the product gas is carbon monoxide. The anode reaction is



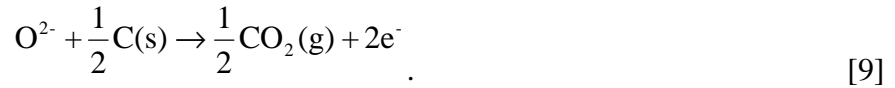
and the cathode reaction is



If the product gas is carbon dioxide, then the overall reaction is



and the anode reaction is

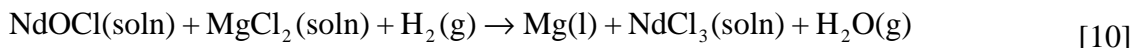


If one assumes that the 16000 C of charge (Figure 4) was passed with 100% current efficiency, then the expected yield of magnesium metal is 2.0 g, which would occupy a volume of approximately 1.2 cm³. As for the anode reactions, 2.3 g of CO is expected (Eq. [6]), or 1.8 g of CO₂ (Eq.[9]). Since the weight loss was greater than this, approximately 7 g rather than 2 g, it seems likely that some volatilization of MgCl₂ occurred during the experiment, in spite of the tight-fitting graphite crucible cover. It is also possible that some of the product metal left the crucible as metal vapor, depositing higher in the tube furnace as a magnesium compound (e.g. MgCl₂ or MgO).

The melt is an ionic conductor, while the remaining components of the current-carrying path are electronic conductors. In the melt, the cations are Mg²⁺ and Nd³⁺. The anions are Cl⁻ and O²⁻. Under the influence of the electric field, the cations move toward the cathode, and the anions move toward the anode. The electrolyte can be visualized as comprising three regions. The region around the anode is the anolyte. The region around the cathode is the catholyte. The third region is the main/bulk electrolyte. If two Faradays of electric charge are passed through the cell, one gram equivalent of magnesium is removed from the catholyte (Eq. [7]), and one gram equivalent of oxygen (Eq. [6] or [9]) is removed from the anolyte. To maintain local charge neutrality, charged species must move in the molten electrolyte. The cationic transport number, n_c , and the anionic transport number, n_a , must sum to unity; the transport numbers represent the fraction of current carried by the two types of ions. From the anolyte, n_c gram equivalents of Mg²⁺ or Nd³⁺ move into the main electrolyte and then into the catholyte. From the catholyte, n_a gram equivalents of Cl⁻ or O²⁻ move into the main electrolyte and then into the anolyte. It is likely that the transport number for chlorine in the melt is nearly unity, so that after passing significant DC current, one should find the concentration of Cl⁻ in the anolyte to be higher than at the beginning of the experiment. As O²⁻ is removed from the anolyte, Cl⁻ will move in to the anolyte to maintain electroneutrality. Also, we should find the concentration of Cl⁻ in the catholyte to be lower than at the beginning of the experiment; as Mg²⁺ is removed from the catholyte, Cl⁻ will move out of the catholyte to maintain electroneutrality.

B. Experiment #2

Electrolysis of the melt should yield magnesium metal, according to the following overall reaction.



Hydrogen gas in a N₂-5 vol% H₂ gas mixture flowing over the cermet coating should react with oxygen anions extracted through the YSZ membrane from the melt; the water vapor produced is flushed out of the YSZ tube by the flow of N₂-5% H₂. The anode reaction is



and the cathode reaction is



Figure 12 is a schematic of the SOM process for magnesium production from a MgCl₂-NdOCl melt. If one assumes that the 3350 C of charge (Figure 7) was passed with 100% current efficiency, then 0.42 g of magnesium metal is expected, which would occupy a volume of 0.24 cm³.

In this experiment, a low temperature (approx. 690°C) was employed primarily to reduce volatilization of magnesium metal, and secondarily to reduce volatilization of MgCl₂ from the electrolyte. This allowed the investigators to prove that SOM technology can be used to produce liquid magnesium from magnesium oxide. Experiments were conducted at higher temperatures (up to 1050°C), but collection of the product magnesium vapor proved difficult in the lab-scale set-up employed. Nevertheless, since the SOM technology involves use of an oxygen-ion-conducting membrane, and the diffusivity of oxygen ions is strongly dependent on temperature, some commercial producers may want to operate at a high temperature (approx. 1050°C), close to that used in solid-oxide fuel cells used for primary power generation. A comparison of operation at different temperatures is provided in Table 6.

A scaled-up version of the technology demonstrated in experiment #2 would have a number of advantages over existing magnesium-production technologies. First, it would be continuous. At regular intervals, MgO would be added, and liquid Mg tapped. If magnesium vapor is produced, then it would be periodically collected from a condenser. Second, MgO feedstock could be used. Magnesium oxide is readily available, and is much easier to store and handle than MgCl₂. Upon addition to the melt, MgO reacts with NdCl₃ in the molten electrolyte to form NdOCl, which is then broken down leading to regeneration of NdCl₃. Third, H₂O vapor is produced at the anode, rather than Cl₂ (conventional MgCl₂ electrolysis) or CO₂ (rare-earth-chloride-based process).^[3]

The presence of the O²⁻-conducting membrane between the melt and the cermet anode ensures that the anode reaction is the oxidation of O²⁻. In order to produce magnesium metal at the cathode, Mg²⁺ cations must be the most noble cations in the melt. Selection of the melt is based on the several other factors also. It is desirable for MgO to have high solubility in the melt. It is also desirable for the melt to have low liquidus temperature, low viscosity, and low

vapor pressure. Finally, there should be insignificant reaction between the melt and the cathode, and between the melt and the solid oxygen-ion-conducting membrane.

V. Conclusions and Suggestions for Further Work

Experiment #1 in the present study sought to improve upon the results obtained in a recent study.^[10] Magnesium metal with Nd content less than 1 wt% was obtained by electrolysis of a $\text{MgCl}_2\text{-NdOCl}$ melt, which proves that liquid Mg can be obtained from a $\text{MgCl}_2\text{-NdCl}_3\text{-MgO}$ melt using a graphite anode and graphite cathode. Co-deposition of Nd with Mg does not appear to be a problem. Experiment #2 was a proof-of-concept experiment that showed that SOM technology can be used to produce Mg from MgO. For this demonstration, the same $\text{MgCl}_2\text{-NdOCl}$ melt was used as in experiment #1, although a large number of other melts may be possible. Future work on the SOM process may be aimed at development of alternative molten electrolyte compositions, studying the thermal and chemical stability of YSZ in various electrolytes, and increasing anode current density. A final comparison of the various magnesium-production methods discussed in this paper may be helpful at this stage. Table 7 compares the conventional process, the U.S. Bureau of Mines process, the process based on rare-earth chlorides, and the solid-oxide oxygen-ion-conducting membrane process.

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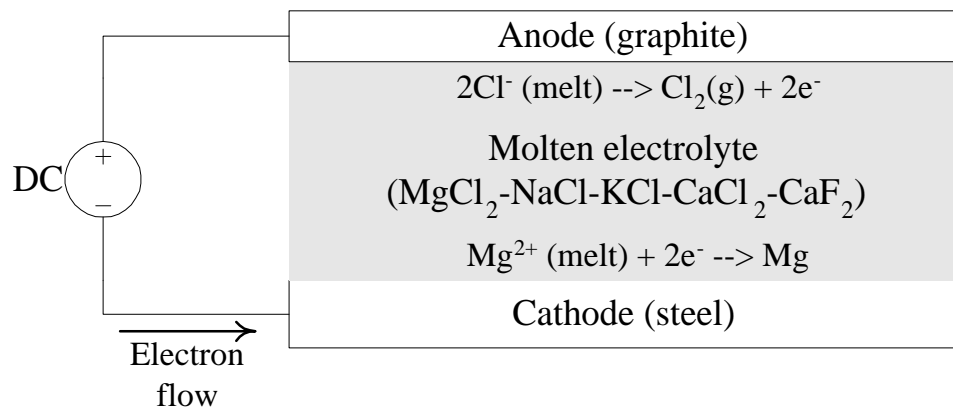


Figure 1. Schematic of cell employed during conventional MgCl_2 electrolysis

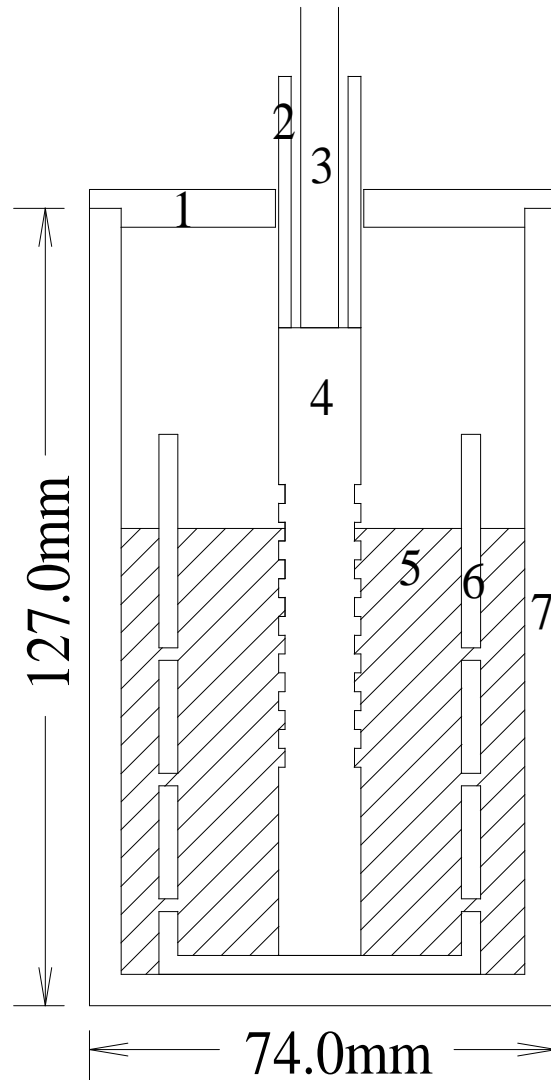


Figure 2: Schematic of apparatus for electrolysis (graphite cathode and graphite anode). 1-graphite crucible cover, 2-alumina separator tube, 3-steel cathode rod, 4-graphite cathode rod, 5- $\text{MgCl}_2\text{-NdOCl}$ melt, 6-MgO separator crucible, 7-graphite crucible (anode).

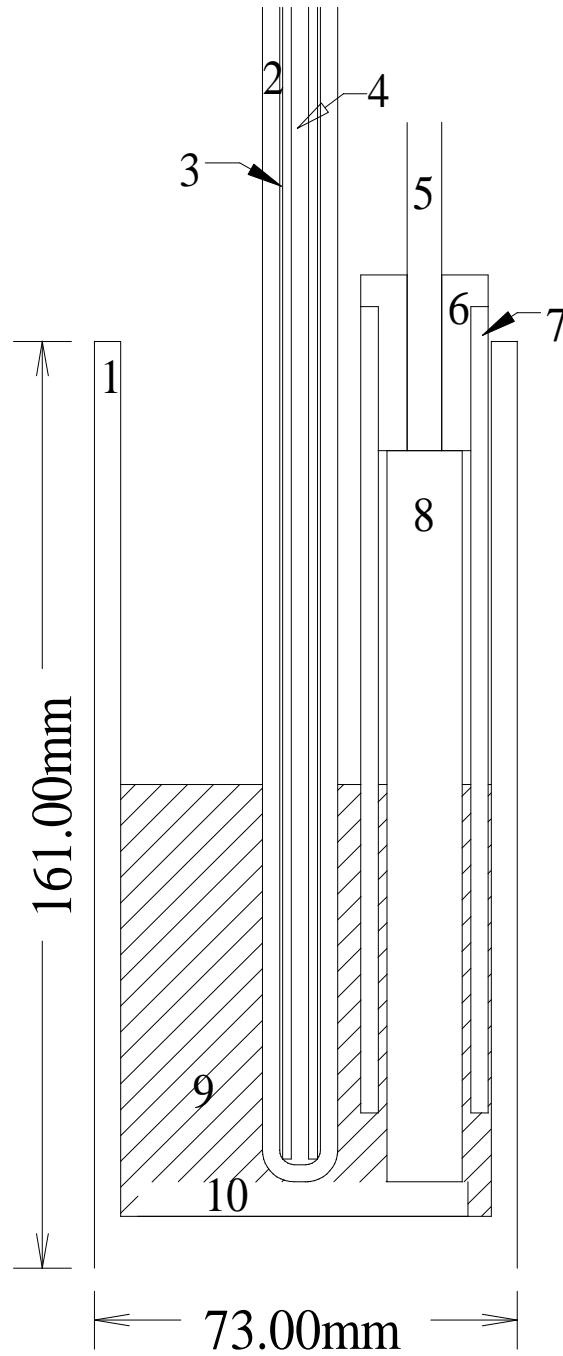


Figure 3: Schematic apparatus for electrolysis by SOM method (graphite cathode and Ni-YSZ anode with YSZ membrane). 1-graphite crucible, 2-YSZ tube (bottom-end-closed), 3-Ni-YSZ cermet coating, 4-stainless steel anode tube, 5-steel cathode rod, 6-graphite plug, 7-MgO separator tube, 8-graphite cathode rod, 9-MgCl₂-NdOCl melt, 10-MgO separator disc.

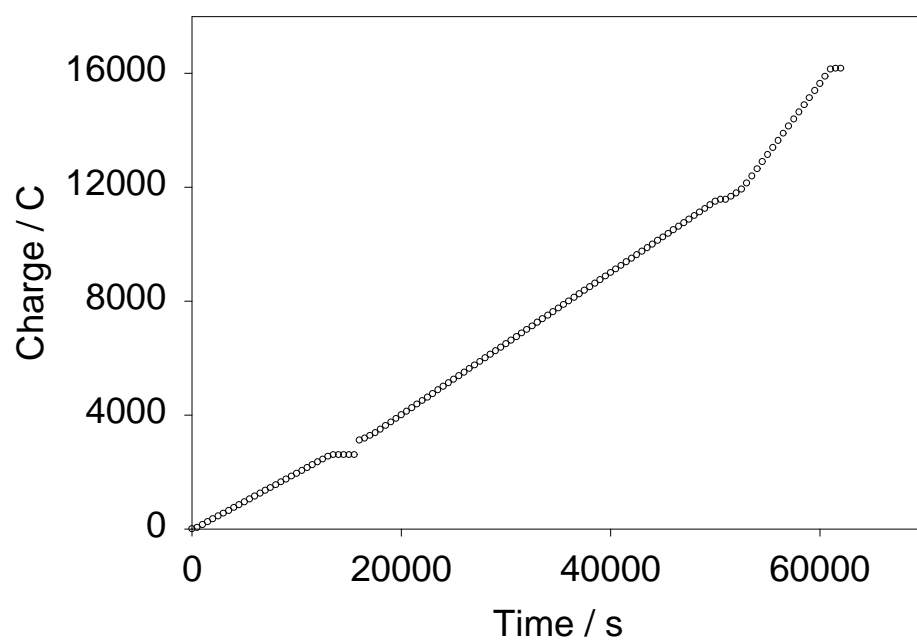


Figure 4. Charge passed through cell during experiment #1.

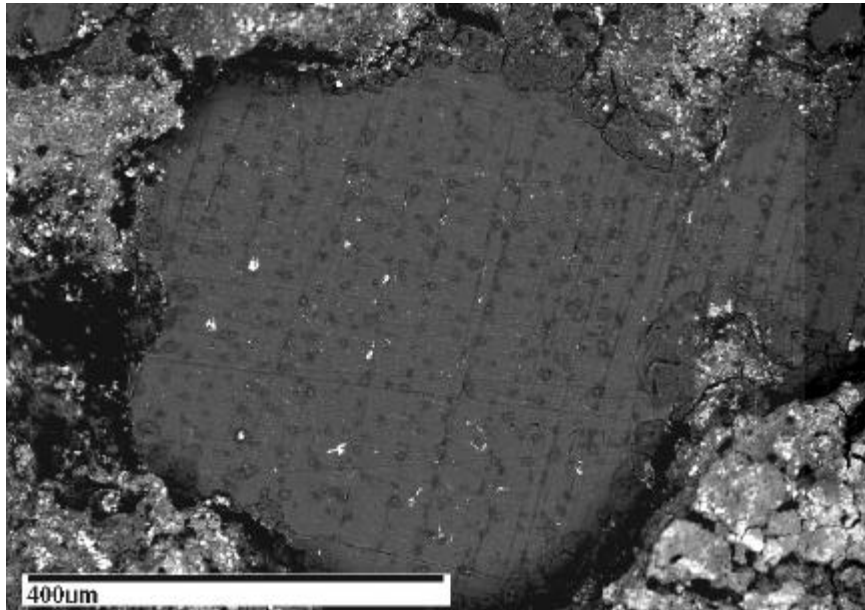


Figure 5. Backscattered electron image of a metal globule from experiment #1

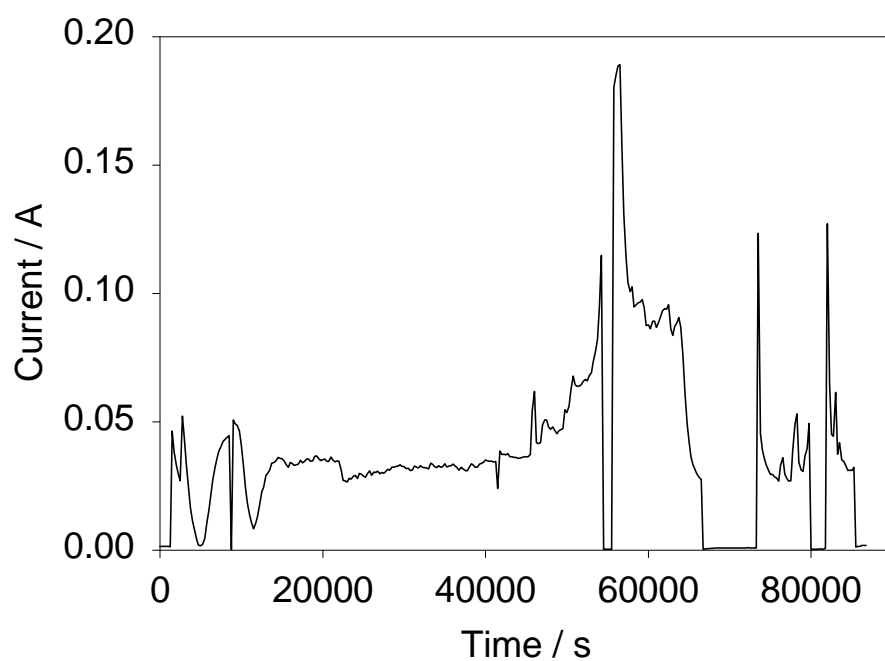


Figure 6. Current recorded as a function of time during experiment #2. A number of current-interruption experiments were conducted during the experiment.

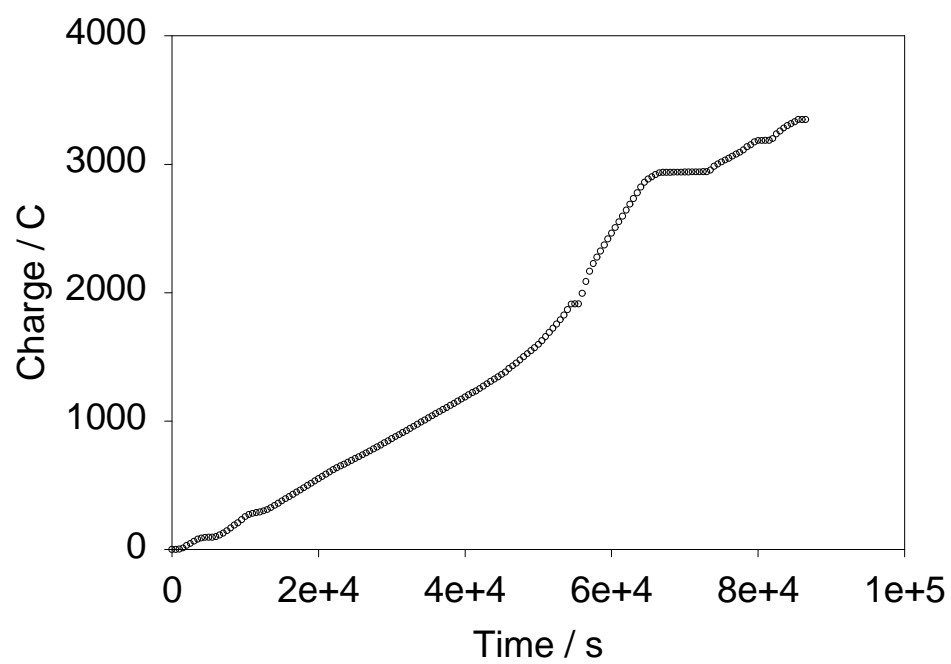


Figure 7. Charge passed through cell during experiment #2

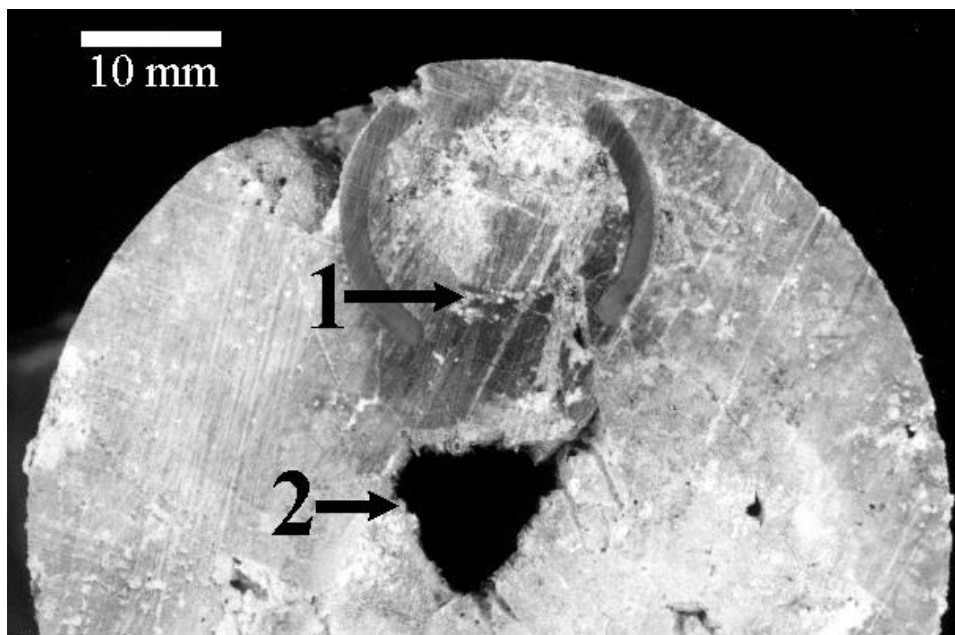


Figure 8. Bottom of frozen melt, revealing notched MgO tube. Key: 1--magnesium metal globules on cathode; 2--crater where anode assembly had been.

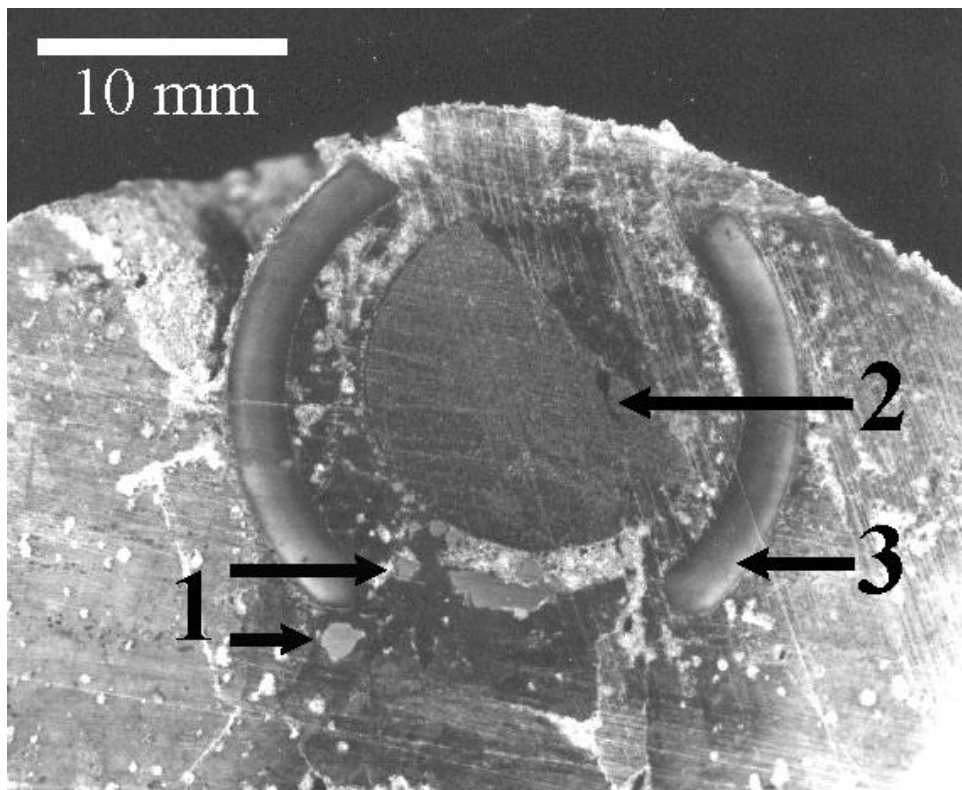


Figure 9. Bottom of frozen melt, revealing magnesium metal globules (#1), graphite cathode rod (#2), and notched MgO tube (#3).

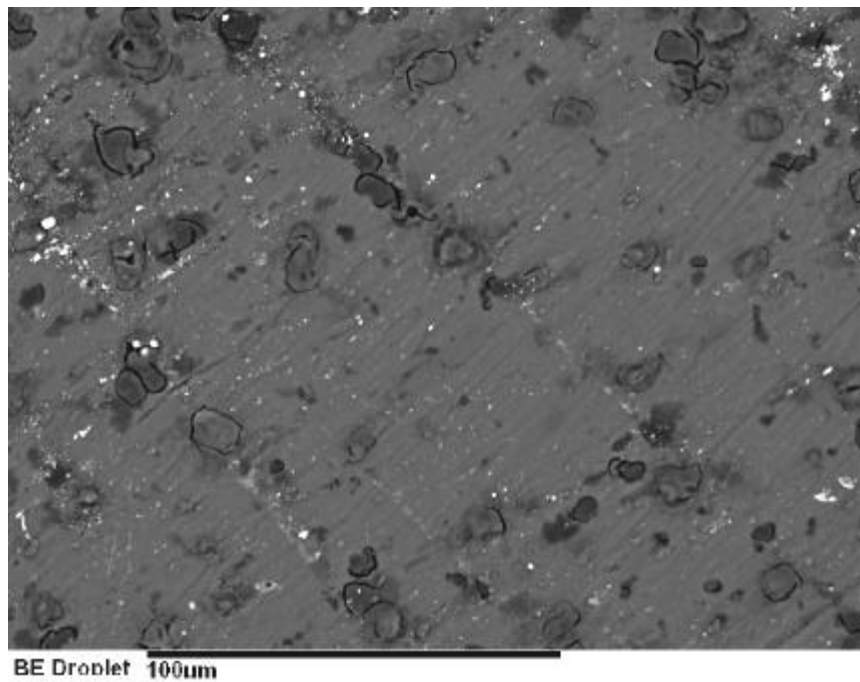


Figure 10. Backscattered electron image of metal globule from experiment #2

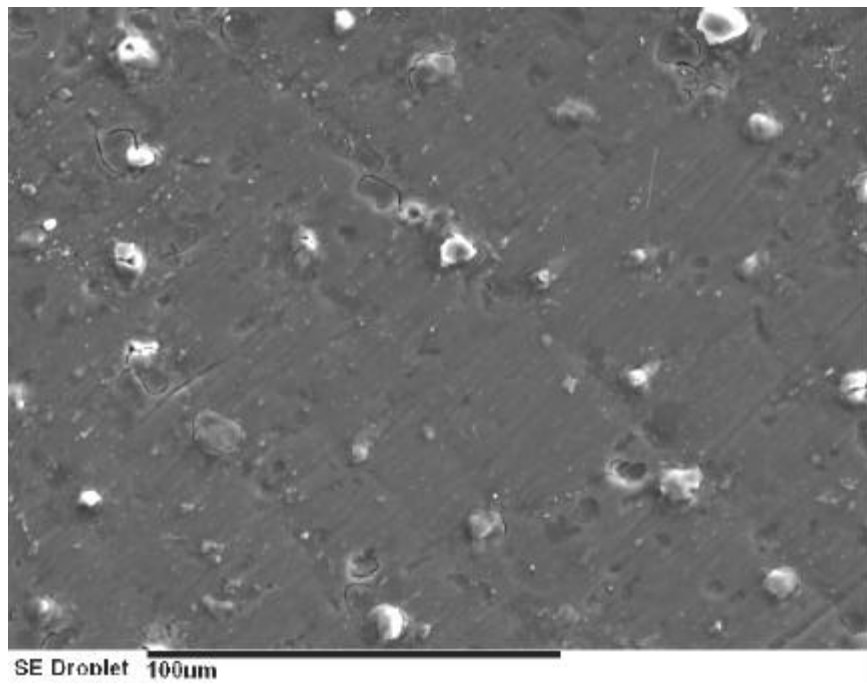


Figure 11. Secondary electron image of metal globule from experiment #2

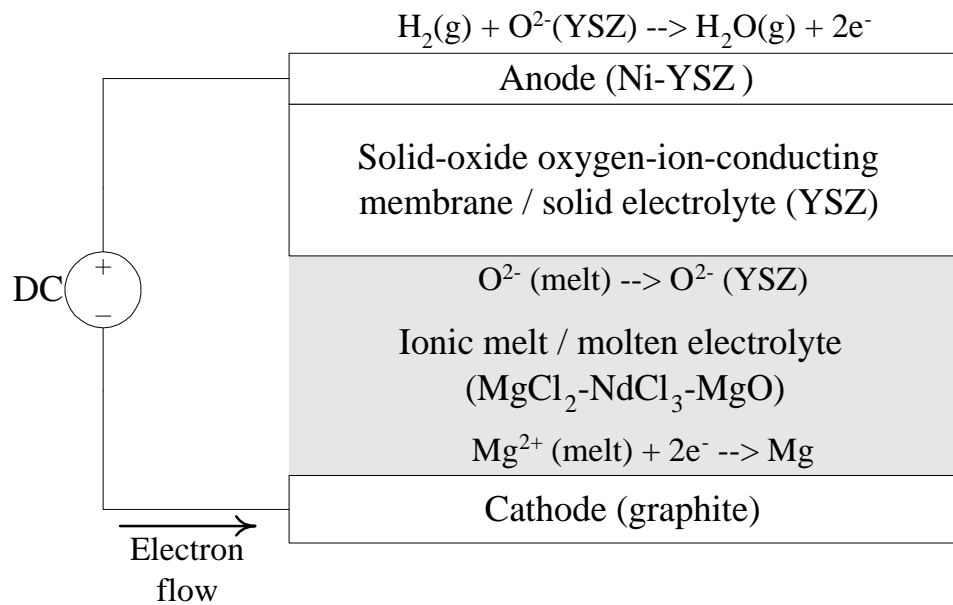


Figure 12: SOM process for Mg production by direction reduction of MgO.

Table 1. Summary of some recent U.S. patents on use of MgO assigned to General Motors

U.S. Patent No.	Unique aspects
5,279,716	<ul style="list-style-type: none">• production of Mg-Nd alloy with approximately 1 wt% Nd (minimum) using electrolytic process based on chloride electrolyte• use of MgO feedstock by reaction with NdCl_3 and other rare earth chlorides• elimination of MgO impurity (MgCl_2 feed) and MgO sludge from cell
5,395,487	<ul style="list-style-type: none">• electrolytic regeneration of electrolyte for demagging of Al-Mg alloys by reaction of MgO with NdCl_3 and other rare earth chlorides
5,427,657	<ul style="list-style-type: none">• production of Mg-Nd alloy with approximately 10-15 wt% Nd using electrolytic process based on fluoride electrolyte• use of MgO feedstock by reaction with NdF_3 and other rare earth fluorides• method for reducing Nd content of Mg-Nd alloys from 15 wt% to <1 wt%
5,593,566	<ul style="list-style-type: none">• cell design with liquid Mg-Al cathode that lies beneath the molten electrolyte• production of Mg-Al alloy (unipolar design) or pure Mg (bipolar design)• elimination of MgO impurity from MgCl_2 feed by reaction with Cl_2
5,665,220	<ul style="list-style-type: none">• elimination of MgO impurity from MgCl_2 feed by sparging anode with Cl_2 and H_2 or with Cl_2 and CH_4• method for producing anhydrous MgCl_2 by sparging with Cl_2-H_2 or Cl_2-CH_4 gas mixtures• method for reducing consumption of carbon anodes in aluminum-producing cell (Hall-Heroult) by sparging anode with Cl_2 and H_2 or with Cl_2 and CH_4
5,853,560	<ul style="list-style-type: none">• new electrolytes based on MgF_2-CaF_2-LiF system that can be used with impure MgCl_2 feed (i.e. containing MgO)• new electrolyte based on MgF_2-CaF_2-CaCl_2 system that can be used with impure MgCl_2 feed (i.e. containing MgO)• new electrolyte based on MgF_2-LiF-LiCl system that can be used with impure MgCl_2 feed (i.e. containing MgO)

Table 2. Chemical and electrochemical reactions that take place during production of magnesium metal from MgCl₂-MgO feedstock^[8]

MgF ₂ -CaF ₂ -LiF electrolyte with MgCl ₂ -MgO feed	MgF ₂ -CaF ₂ -CaCl ₂ electrolyte with MgCl ₂ -MgO feed
MgCl ₂ feedstock $\text{MgCl}_2 + 2 \text{LiF} = \text{MgF}_2 + 2 \text{LiCl}$ $2 \text{LiCl} = 2 \text{Li} + \text{Cl}_2$ (electrolysis) $2 \text{Li} + \text{MgF}_2 = 2 \text{LiF} + \text{Mg}$	MgCl ₂ feedstock $\text{MgCl}_2 + \text{CaF}_2 = \text{MgF}_2 + \text{CaCl}_2$ $\text{CaCl}_2 = \text{Ca} + \text{Cl}_2$ (electrolysis) $\text{Ca} + \text{MgF}_2 = \text{Mg} + \text{CaF}_2$
MgO feedstock $2 \text{MgO} + \text{C} = 2 \text{Mg} + \text{CO}_2$ $\text{MgO} + 2 \text{LiF} + \text{Cl}_2 = \text{MgF}_2 + 2 \text{LiCl} + 1/2 \text{O}_2$	MgO feedstock $2 \text{MgO} + \text{C} = 2 \text{Mg} + \text{CO}_2$ $\text{MgO} + \text{CaF}_2 + \text{Cl}_2 = \text{MgF}_2 + \text{CaCl}_2 + 1/2 \text{O}_2$

Table 3. Data from experiment #1 (graphite anode and graphite cathode)

Time period (hours:minutes)	Current applied (A)	Voltage measured (V)	Charge (C)
03:36	0.20	1.89-2.08	2592
00:20	0.20	1.10-1.79	240
09:06	0.25	1.90-1.96	8190
00:22	0.25	1.81-1.91	330
02:22	0.50	2.13-2.16	4260

Table 4. Electrode-melt areas, and current densities

Expt #	Anode-melt area (cm ²)	Anode current density (mA cm ⁻²)	Cathode-melt area (cm ²)	Cathode current density (mA cm ⁻²)
1	140	1.5-3.6 *	29	6.9-17 *
2	27	1.5-7.0 **	28	1.4-6.8 **

* Steady state current was in range 0.20-0.50 A during this galvanostatic experiment.

** Steady state current was 0.04 A, and highest peak current (after current interruption) was 0.19 A during this potentiostatic experiment.

Table 5. Temperature readings after raising anode assembly at end of experiment #2

Elapsed time (minutes)	Thermocouple reading (°C)
0	665
5	647
10	629
15	611
20	594

Table 6. Comparison of SOM process for magnesium production, operated at different temperatures.

Low temperature (approx. 750°C)	High temperature (approx. 1050°C)
Advantages: <ul style="list-style-type: none"> • relatively large heating requirement • low rate of melt volatilization 	Advantages: <ul style="list-style-type: none"> • lower cell potential (high O^{2-} diffusivity in membrane) • natural gas may be used at the anode
Disadvantages: <ul style="list-style-type: none"> • higher cell potential (low O^{2-} diffusivity in membrane) 	Disadvantages: <ul style="list-style-type: none"> • relatively large heating requirement * • high rate of melt volatilization

* The process may be self-sustaining after heat-up.

Table 7. Comparison of processes for magnesium production

Process	Temperature (°C)	Source of Mg metal	Anode consumed?	Can accept MgO feed?	Uses conventional electrolytic cell?	Sludge forms?	Product at anode
Conventional	700-740	MgCl ₂ [†]	yes -- by reaction with H ₂ O and MgO	no -- MgO sludge would rapidly form	yes	yes -- due to water in MgCl ₂ feed	Cl ₂ gas
US Bureau of Mines ^[2]	800-815	MgO	yes -- by reaction with MgO	yes -- although anode is consumed	yes	yes -- addition excess MgO excess necessary	CO ₂ and Cl ₂ [‡]
Rare earth chloride ^[3]	700-740	MgO or MgCO ₃	yes -- by reaction with MgO	yes -- although anode is consumed	yes	no [§]	CO ₂ and Cl ₂
SOM process	700-1100	MgO or MgCO ₃	no	yes	no ^{**}	no [§]	H ₂ O

* Carbon anode and steel or iron cathode.

† Magnesium chloride must be purified and dried before adding to electrolytic cell; if water is introduced, then it reacts with the carbon anode (forming CO₂) or with MgCl₂ (forming MgO). Use of MgO eliminates several processing steps associated with MgCl₂ preparation.

‡ Addition of excess MgO reduces evolution of Cl₂.

§ NdOCl may precipitate if solubility limit in MgCl₂-NdCl₃ is exceeded.

** YSZ membrane and Ni-YSZ anode cermet are used.