This paper reports a solid oxide membrane (SOM) electrolysis process using an LSM (La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3\)-Inconel inert anode current collector and liquid silver anode for production of aluminum and oxygen from aluminum oxide dissolved in a pre-selected molten oxy-fluoride flux containing Ca, Mg, Al and Y at 1473K (1200°C). The electrochemical behavior of the SOM cell was characterized by various electrochemical techniques including electrochemical impedance spectroscopy, potentiodynamic scan and potentiostatic electrolysis. Based on the electrochemical measurement results, an equivalent circuit model of the SOM electrolysis process is presented. A polarization model for aluminum and oxygen production was developed and the polarization losses in the cell were analyzed according to the equivalent circuit. Based on the polarization model analysis, potential approaches to improve the cell performance are also discussed. The aluminum produced and the yttria stabilized zirconia (YSZ) membrane were characterized with scanning electron microscope and energy-dispersive X-ray spectroscopy after the electrolysis.

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Manuscript submitted December 12, 2016; revised manuscript received January 18, 2017. Published January 31, 2017.

Solid oxide membrane (SOM) electrolysis is a novel metals extraction technique that is being developed for the production of several energy-intensive metals, semiconductors or alloys, such as Mg, Ti, Ta, Yb, Si, CeNi\(_5\) and Ti-Fe alloy. The SOM electrolysis process features the utilization of an oxygen-ion-conducting membrane, typically made of yttria-stabilized zirconia (YSZ), for directly electrolyzing metal oxides dissolved in a pre-selected non-consumable molten flux. An LSM (La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3\)-Inconel inert anode current collector and liquid silver anode have been used in SOM electrolysis process for oxygen evolution. The aluminum that was produced in the process was characterized by scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS). The YSZ membrane stability during the electrolysis was also studied in order to assess the membrane stability for long-term aluminum production.

**Experimental**

**SOM electrolysis setup.**—Figure 1 shows the schematic of a SOM electrolysis setup. The setup consists of a grade 304 stainless steel (SS-304) crucible that was heated to 1473 K in forming gas (95% Ar:5% H\(_2\)) to ensure an inert atmosphere. Inside the crucible, 450g of powdered flux (45 wt% MgF\(_2\) – 55 wt% CaF\(_2\) containing 6 wt% CaO, 3 wt% Al\(_2\)O\(_3\) and 4 wt% YF\(_3\)) was used to form the molten electrolyte. A one-end-closed 6 mol% YSZ membrane tube separated the flux from 44 g of liquid silver enclosed inside the YSZ tube. An LSM-Inconel inert anode current collector was disposed in the YSZ tube and was submerged in the liquid silver anode. The structure of the anode assembly is described in our previous work on Mg production from MgO using the Mg-SOM electrolysis cell. An Al\(_2\)O\(_3\) dielectric tube served as a cathode separator as well as a source of Al\(_2\)O\(_3\). Because liquid aluminum is less dense than the molten flux, the aluminum produced during the electrolysis floats on top of the molten flux and is easily confined within the dielectric tube. This prevents the aluminum from spreading on the surface of the flux and shorting the cell. The Al\(_2\)O\(_3\) dielectric tube was inserted in a stainless steel support welded to the bottom of the stainless steel crucible. The stainless steel support had multiple opening at the side to allow flux to go through
the support and contact with the cathode. The powdered flux was pre-melted in the stainless steel crucible with the \( \text{Al}_2\text{O}_3 \) tube inserted in the stainless steel support prior to the electrolysis. The cathode material was TiB\(_2\), which is a conductive ceramic that wets but does not alloy with liquid aluminum.\(^{23}\) The top half of the cathode TiB\(_2\) bar was inserted in a stainless steel crucible, which was welded to a stainless steel rod. The stainless steel rod served as the cathode current collector. The stainless steel crucible contained a layer of liquid silver that made contact with the TiB\(_2\) bar. The liquid silver layer ensured that the contact resistance between the stainless steel crucible and the TiB\(_2\) bar was minimized. During the electrolysis, the stainless steel crucible stayed above the molten flux. A boron nitride cover supported by an alumina pin prevented aluminum from climbing up the TiB\(_2\) bar. During the electrolysis, the TiB\(_2\) cathode current collector was inserted in the molten flux (see the detailed cathode design in Figure 1). A stainless steel alternative electrode was inserted in the molten flux to monitor the electrochemical behavior of the flux during the electrolysis. The alternative electrode was electrically insulated by an alumina tube, which also served as a gas stirring tube. The electrical resistance of the molten flux between the cathode and the alternative electrode was measured after the electrolysis to assess whether the flux remained primarily ionic. To facilitate chemical homogeneity in the molten flux, a layer of liquid silver was passed through the stirring tube at 20 cm\(^3\)/min.

**Chemicals and materials.**—Magnesium fluoride hydrate (\( \text{MgF}_2 \cdot x\text{H}_2\text{O} \) min. 87\% \( \text{MgF}_2 \)), calcium fluoride (99.5\%), calcium oxide (reagent grade), aluminum oxide (99\%), yttrium (III) fluoride (99.9\%) and aluminum shots (99.5\%) were supplied by Alfa Aesar (Ward Hill, MA, USA). The powders were dried for 4 hours at 673 K to remove moisture and crystallized water. The powders were then dry mixed in a ball mill overnight according to the flux stoichiometry. The closed one end YSZ tube (6 mol\% \( \text{Y}_2\text{O}_3 \), 1.90 cm o.d., 1.27 cm i.d., 60.96 cm length) was supplied by McDanel (Beaver Falls, PA, USA). The alumina stirring tubes and the cathode alumina sleeve were supplied by CoorsTek (Golden, CO, USA). The forming gas was supplied by Airgas (Billerica, MA, USA). The boron nitride cover was machined from a boron nitride plate supplied by Saint-Gobain (Malvern, PA, USA). The titanium diboride was machined by wire-cut electrical discharge machining (EDM) to the desired shape.

**Design of the molten flux.**—The components in the molten flux and their composition are designed to have high ionic conductivity, high alumina solubility and be chemically compatible with the YSZ membrane. The non-aluminum cations in the molten flux should be less electronegative than \( \text{Al}^{3+} \) so that during the electrolysis they remain in the flux and not get reduced. \(^{45} \% \text{MgF}_2 \) – 5\% \( \text{CaF}_2 \) is a eutectic composition having a melting temperature of 1247 K.\(^{24}\) It has been used as the base flux composition for Mg production process using SOM electrolysis.\(^{10,16–20}\) It is known to have high ionic conductivity and is chemically compatible with the YSZ membrane.\(^{25,26}\) However, the \( \text{Al}_2\text{O}_3 \) dissolved in the flux lowers the optical basicity of the flux and thereby has a tendency to corrode the YSZ membrane. \( \text{CaO} \) was added in the flux in order to increase the optical basicity of the flux and match it with that of the YSZ membrane so that the flux is stable in contact with the YSZ membrane.\(^{27–32}\) The \( \text{CaO} \) also helps to break the \( \text{Al}-\text{O}-\text{F} \) polymeric network, and thereby increase the alumina solubility in the flux. \( \text{YF}_3 \) was added to prevent yttrium depletion from the YSZ membrane and increase membrane stability.\(^{25,33}\) Both \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) are less electronegative than \( \text{Al}^{3+} \) at 1473 K,\(^{34}\) therefore they are expected to remain in the melt as long as the \( \text{Al}^{3+} \) concentration near the cathode does not drop to low levels due to concentration polarization.

**Electrochemical characterization of electrolysis process.**—The electrochemical characterization of the SOM cell was performed between the LSM-Inconel inert anode current collector and the stainless steel rod cathode current collector. The potentiodynamic scans (PDS) were performed at 5 mV/s using a Solartron SI 1280B electrochemical measurement system in order to determine the dissociation potentials of \( \text{Al}_2\text{O}_3 \) and that of the less stable impurity oxides present in the flux. The electrochemical impedance spectroscopy (EIS) scans were performed using a Princeton Applied research 263A potentiostat and a Solartron 1250 frequency response analyzer to determine the ohmic resistance of the SOM cell. The impedance scans were from 20000 to 1 Hz with 20 mV amplitude. The ohmic resistance of the measured
The electrolysis experiments were performed using an Agilent Technologies N5743A power source. When the applied DC potential exceeded the dissociation potential of $\text{Al}_2\text{O}_3$, Al was produced at the cathode, and $\text{O}_2$ evolved at the liquid silver anode. The overall cell reaction can be written as:

$$\text{Al}_2\text{O}_3 = 2\text{Al}(l) + \frac{3}{2}\text{O}_2(g) \quad [1]$$

The anode exit gas (oxygen) flow rate during the electrolysis was measured by passing it through a FMA-4305 digital flowmeter (OMEGA Engineering, CT, USA). The measured oxygen flow rate was used to calculate the ionic current involved in producing aluminum from alumina. The current efficiency was determined as the ratio of the ionic current for producing aluminum to the total current that passed through the cell. It is to be noted that the flow rate of the oxygen could not be measured by the digital flowmeter until the oxygen saturated the liquid silver anode, which is dependent on the amount of silver and the ionic current. Typically, for our electrolysis experiments it took about an hour for the silver to saturate before the oxygen flow rate could be measured in the anodic exit gas.

Post-experimental characterization.—After the SOM electrolysis experiment, the setup was disassembled for detailed analysis. A piece of flux sample near the cathode containing the aluminum product and a piece of YSZ membrane were mounted in epoxy, polished, coated with carbon, and then characterized using a Zeiss supra 55VP field emission scanning electron microscope (SEM). The purity of the aluminum produced at the cathode was measured by energy-dispersive X-ray spectra (EDS) quantitative analysis. The yttrium and zirconium content in the YSZ membrane were measured by EDS line scan to assess membrane stability after the electrolysis.

Results and Discussion

SOM electrolysis runs.—Electrolysis was performed with an applied DC potential of 2.75 V between the cathode and the anode for 24 hours. The electrolysis was performed potentiostatically to control and stabilize the potential drop profile across the cell, which helps minimize the reduction of all spectator cations and protects the YSZ membrane from $\text{ZrO}_2$ dissociation throughout the electrolysis. The current and the current efficiency during the electrolysis were continuously monitored (see Figure 2). The current efficiency started at 90% and decreased to 70% over time. The electrolysis was stopped when the current efficiency dropped below 70% because of electronic conductivity in the flux. This is likely due to dissolution of magnesium in the flux that is reduced at the cathode because of alumina concentration polarization. The SOM cell was then held at the operating temperature for 1.5 hours to allow the magnesium to evaporate from the flux or react with the alumina in the flux.

After the cell was equilibrated, a second electrolysis with an applied potential of 2.75 V was performed for ~3 hours (see Figure 3).

Current-potential characteristics of the SOM cell.—A Potentiodynamic scan (PDS) (5 mV/s) was performed from 0.3 V to ~3.25 V after the first electrolysis to determine the dissociation potential of $\text{Al}_2\text{O}_3$ and to identify impurity dissociation of any other oxides after the 1$^{st}$ electrolysis (see Figure 4). The initial negative current indicates reverse electrolysis reaction, because the applied voltage was smaller than the Nernst potential of the SOM cell. The only dissociation potential identified from the PDS was at 2.10 V which appears to correspond to the Nernst potential (2.08 V) for the reaction $\text{Al}_2\text{O}_3 = 2\text{Al}(l) + \frac{3}{2}\text{O}_2(g)$ at 1473 K. This indicates that all impurity cations were dissociated during the first electrolysis. The leakage electronic current before alumina dissociation was negligible, indicating that the flux was primarily ionic.

Ohmic resistance of the SOM cell.—Two EIS scans were performed between the cathode and the anode, one before the first electrolysis and the other after the second electrolysis. The high-frequency intercept on the Nyquist plots before and after the electrolysis (Figure 5) showed that, the total ohmic resistance of the cell was around $0.76 \Omega$ prior to the electrolysis and increased slightly to $0.85 \Omega$.
after the electrolysis, indicating that the electrical properties of the flux did not change very much. It is noted that the difference in polarization resistance between two EIS scans were due to the cathode environment change before and after the electrolysis. The aluminum produced during the electrolysis wetted and coated the TiB₂, subsequently changed the electrocatalytic activity of the interface between the cathode and the flux. The EIS scan between the cathode and the stainless steel alternative electrode after the electrolysis showed that the ohmic resistance of the flux between the two electrodes was 0.69 Ω. This also suggests that the molten flux was primarily ionic after the electrolysis.

Post-experimental characterization.—The furnace was cooled after the SOM electrolysis experiment, and the setup was disassembled. Aluminum was found inside the cathode alumina tube as shown in Figure 6. Quantitative analysis of the EDS spectrum (Figure 7) showed that the product was primarily Al-Mg alloy with 94 wt% Al. MgO activity in the flux is due to the presence of Mg²⁺ and O²⁻ ions, and its reduction results in the dissolution of Mg in the aluminum. Mg is a common additive in Al alloys which can increase its strength. The amount of Mg in the Al product can also be easily tailored by boiling off the existing Mg or by adding additional Mg.

The YSZ membrane stability was characterized after the electrolysis using SEM image and EDS line scan (Figure 8). It is shown from the line scan that the flux did not attack the YSZ membrane during the electrolysis. The yttrium and zirconium contents were uniform along the YSZ membrane. The ratio of yttrium and zirconium was similar to as received YSZ membrane. No electrolyte corrosion was observed. It was confirmed that the YSZ membrane was chemically and electrochemically stable after 28 hours of electrolysis.

Modeling

Equivalent circuit modeling.—In order to fully understand the electrochemical behavior of the SOM cell and provide insights into decreasing the polarization losses in the cell, it is crucial to develop an electrochemical model for the SOM cell. Equivalent circuit modeling is a useful tool to model the SOM electrolysis process. Guan et al. has developed a generic equivalent DC circuit model that takes into account all the known mechanisms associated with the current flow including (1) the dissociation of the desired oxide, (2) the dissociation of impurity oxides, (3) electronic conductivity of the molten flux, and (4) the various resistive contributions of the SOM cell. A similar equivalent DC circuit of the SOM electrolysis for Al production is proposed in Figure 9. The symbols used in Figure 9 are defined in Table 1.
According to the simplified equivalent circuit (Figure 10), the applied potential is unlikely during the electrolysis. Therefore, the cathode is very low. Because of the two reasons listed above, the depolarization, and

\[ \eta = \frac{E_{2} - E_{1}}{nF} \]

where \( E_{2} \) is the absolute value of the Nernst potential for aluminum production, \( E_{1} \) is the applied potential, and \( n \) is the number of electrons involved.

Nernst potential for Al\(_2\)O\(_3\) dissociation.—The Nernst potential for Al\(_2\)O\(_3\) dissociation is given by

\[ E_{N, Al_{2}O_{3}} = E_{N, Al_{2}O_{3}}^0 + \frac{RT}{nF} \ln \left( \frac{a_{Al_{2}O_{3}}}{a_{Al_{2}O_{3}}^{anode}} \right)^{3/2} \]

Polarization model of the SOM cell for aluminum production.—According to the simplified equivalent circuit (Figure 10), the applied potential \( E_{applied} \) can be written as:

\[ E_{applied} = E_{N, Al_{2}O_{3}} + \eta_{ohm} + \eta_{ct(a,c)} + \eta_{conc, c} + \eta_{conc, a} \tag{2} \]

where \( E_{N, Al_{2}O_{3}} \) is the absolute value of the Nernst potential for alumina dissociation, \( \eta_{ohm} \) is the ohmic polarization of the SOM cell, \( \eta_{ct(a,c)} \) is the charge transfer or the activation polarization (includes both the cathode and the anode), \( \eta_{conc, c} \) is the cathodic concentration polarization, and \( \eta_{conc, a} \) is the anodic concentration polarization.

Table I. Definitions of symbols in the SOM equivalent circuits.

| Symbol | Definition |
|--------|------------|
| \( R_{impurity}^{YSZ} \) | Ionic resistance of YSZ membrane involved for impurity oxides dissociation |
| \( R_{Al_{2}O_{3}}^{YSZ} \) | Ionic resistance of YSZ membrane involved for Al\(_2\)O\(_3\) dissociation |
| \( R_{ZrO_{2}}^{YSZ} \) | Ionic resistance of YSZ membrane involved for ZrO\(_2\) dissociation |
| \( R_{impurity}^{flux} \) | Ionic resistance of flux involved for impurity oxides dissociation |
| \( R_{Al_{2}O_{3}}^{flux} \) | Ionic resistance of flux involved for Al\(_2\)O\(_3\) dissociation |
| \( R_{impurity}^{con(a,c)} \) | Concentration polarization resistance at the anode and cathode for impurity oxides dissociation |
| \( R_{Al_{2}O_{3}}^{con(a,c)} \) | Concentration polarization resistance at the anode and cathode for Al\(_2\)O\(_3\) dissociation |
| \( R_{ZrO_{2}}^{con(a,c)} \) | Concentration polarization resistance at the anode and cathode for ZrO\(_2\) dissociation |
| \( R_{YSZ} \) | Electronic resistance of the YSZ membrane |
| \( R_{e}^{YSZ} \) | Electronic resistance of the flux between YSZ and cathode |
| \( R_{ex} \) | Resistance of external lead wires |
| \( E_{impurity}^{N} \) | Nernst potential for impurity oxides dissociation |
| \( E_{Al_{2}O_{3}}^{N} \) | Nernst potential for Al\(_2\)O\(_3\) dissociation |
| \( E_{ZrO_{2}}^{N} \) | Nernst potential for ZrO\(_2\) dissociation |
| \( E_{applied} \) | Applied potential |
| \( I_{impurity} \) | Ionic current for impurity oxides dissociation |
| \( I_{Al_{2}O_{3}} \) | Ionic current for Al\(_2\)O\(_3\) dissociation |
| \( I_{ZrO_{2}} \) | Ionic current for ZrO\(_2\) dissociation |
| \( I_{e}^{YSZ} \) | Electronic current passing the YSZ membrane |

Figure 8. SEM image and EDS line scan of YSZ membrane after electrolysis. (a) EDS line scan. (b) Quantitative element analysis of the atomic percentage of Y and Zr.

Figure 9. Equivalent DC circuit of the aluminum SOM cell (modified after Ref. 17).
The activity of Al₂O₃ at the interface between the flux and the cathode, where there is little mass-transfer effects, is equal to one. Therefore, the charge transfer reactions at the electrodes. For small currents, the overpotential \( \eta \) is experimentally identified as the deflection point in the current-potential plot obtained using the PDS between the anode and the cathode current collectors.

**Activation polarization.**—The activation polarization \( \eta_{\text{act}} \) is the overpotential required to overcome the activation energy barrier for the charge transfer reactions at the electrodes. For small currents, where there is little mass-transfer effects, \( \eta_{\text{act}} \) is described by the Butler-Volmer equation:

\[
i = i_0 \exp \left( \frac{\alpha n \eta_{\text{act}} F}{RT} \right),
\]

where \( i_0 \) is the exchange current, \( \alpha \) is the transfer coefficient, \( n \) is the number of electrons transferred (\( n = 6 \) for the alumina dissociation), \( F \) is the Faraday constant, and \( T \) is the operating temperature. Assuming a symmetric activation energy barrier for both electrode reactions, the transfer coefficient \( \alpha \) is suggested to be 0.5. Substituting \( n = 6 \) and \( \alpha = 0.5 \) in Equation 6, and solving the equation for \( \eta_{\text{act}} \) as a function of \( i \), the activation polarization can be expressed as:

\[
\eta_{\text{act}} = \frac{RT}{3F} \ln \left[ \frac{i}{2i_0} + \sqrt{\frac{i^2}{4i_0^2} + 1} \right]
\]

**Cathodic concentration polarization.**—The cathodic concentration overpotential \( \eta_{\text{conc}} \) is results from the Al₂O₃ concentration gradient across the diffusion layer at the cathode surface. It can be expressed as follows:

\[
\eta_{\text{conc}} = \frac{RT}{6F} \ln \left( \frac{a_{\text{Al}_2O_3}^\text{flux}}{a_{\text{Al}_2O_3}^\text{cathode}} \right)
\]

where \( a_{\text{Al}_2O_3}^\text{flux} \) is the activity of Al₂O₃ in the bulk of the flux, and \( a_{\text{Al}_2O_3}^\text{cathode} \) is the activity of Al₂O₃ at the interface between the flux and the cathode at a given current density \( i \). Assuming a Henrian solution, Equation 8 can be written as follows,

\[
\eta_{\text{conc}} = \frac{RT}{6F} \ln \left( \frac{C_{\text{Al}_2O_3}^\text{flux}}{C_{\text{Al}_2O_3}^\text{cathode}} \right)
\]

where \( C_{\text{Al}_2O_3}^\text{flux} \) is the concentration of Al₂O₃ in the bulk of the flux, and \( C_{\text{Al}_2O_3}^\text{cathode} \) is the concentration of Al₂O₃ at the interface between the flux and the cathode at a given current density \( i \).

Assuming a linear concentration gradient within the diffusion layer, the diffusive flux of Al₂O₃ at the cathode surface can be expressed by Fick’s first law as follows

\[
\mathbf{J}_{\text{Al}_2O_3} = -D_{\text{Al}_2O_3} \frac{\partial C_{\text{Al}_2O_3}}{\partial x}
\]

where \( D_{\text{Al}_2O_3} \) is the diffusivity of the alumina in the flux, \( C_{\text{Al}_2O_3} \) is the concentration of Al₂O₃ at the interface between the flux and the cathode at a given current density \( i \).
The current-potential curve obtained from the PDS scan can be curve-fitted using Equation 15 to analyze the polarization losses and quantify the unknown parameters.

**Curve fitting of the measured current-potential relationship.**—The current-potential curve obtained after reaching equilibrium following the 1st electrolysis was used for the curve fitting (Figure 4). From the current-potential curve, the dissociation potential of alumina (\(E_{\text{Al}}^{\text{O}_2\text{O}_3}\)) is identified at 2.10 V. The current at 2.10 V (0.06 A) is used as the baseline for the curve fitting. The difference between the measured current and the baseline current is referred as the net current.

The ohmic resistance of the SOM cell (\(R_{\text{cell}}\)) was measured to be 0.70 Ω (see Figure 5). The fitting potential range is chosen to be from 2.10 V to 2.60 V. In this potential range, the current is small and the cathodic concentration polarization is negligible. In addition, mass-transfer-limited behavior was not observed in the PDS. Therefore, the current-potential relationship can be simplified as

\[
E_{\text{applied}} = E_{\text{Al}}^{\text{O}_2\text{O}_3} + i R_{\text{cell}} + \frac{RT}{F} \ln \left( \frac{i}{2i_0} \right) + \frac{RT}{6F} \ln \left( \frac{P_{\text{O}_2(\text{Ag})}}{1 \text{ atm}} \right)
\]

[16]

The parameters used for the curve fittings are: \(R_{\text{cell}} = 0.70 \Omega\), \(E_{\text{Al}}^{\text{O}_2\text{O}_3} = 2.10 \text{ V}\), the operating temperature T, the gas constant R, and the Faraday constant F. The exchange current \(i_0\) and the oxygen partial pressure for bubble formation at the Ag/YSZ interface, \(P_{\text{O}_2(\text{Ag})}\), are the two unknown fitting parameters. The result of the curve fitting is shown in Figure 11.

Based on the curve fitting results, the exchange current, \(i_0 = 0.1129 \text{ A}\), and the oxygen partial pressure for bubble formation at the Ag/YSZ interface \(P_{\text{O}_2(\text{Ag})} = 1.246 \text{ atm}\). This result justifies the assumption that the oxygen bubbles evolve from the liquid Ag only when the oxygen partial pressure exceeds the atmosphere pressure.

When the curve fitting results extend to a wider potential range from 2.1 V to 3.3 V, the deviation between the fitted curve and the PDS scan increases with increasing potential. This is likely due to the cathodic concentration polarization. During the PDS scan, the thickness of the diffusion layer (\(\delta_c\)) keeps increasing, resulting in a non-steady state condition and the cathodic limiting current \(i_{c*}\) cannot therefore be calculated. However, since the curve fitting results are fairly accurate at low potential range (see Figure 10), we can attribute the difference between the PDS measurement potential and the curve fitted potential as the contribution of cathodic concentration polarization at potentials higher than 2.6 V.

**Approaches to improve the cell performance.**—The equivalent circuit modeling and the current-potential curve fitting results suggest that in order to improve the performance of the SOM electrolysis, the cathodic concentration polarization, charge transfer polarization and the ohmic polarization losses need to be reduced. The cathodic concentration polarization can be lowered by either increasing the alumina activity near the cathode or facilitating the mass transfer better near the cathode with gas stirring. Increasing the activity of alumina near the cathode can also lower the Nernst potential for alumina dissociation. The charge transfer polarization loss can be lowered by increasing the electrocatalytic activity of the electrodes (changing the electrode material). The ohmic polarization loss appears to be the most dominant in our system. It can be reduced by decreasing the distance between the cathode and the anode, decreasing the thickness of the YSZ membrane or engineering the flux composition to increase its electrical conductivity.

**Conclusions**

In this paper, the feasibility of producing Al at the cathode and O2 at the anode by electrolyzing aluminum oxide dissolved in pre-selected molten oxy-fluoride flux using SOM electrolysis process has been demonstrated. Laboratory scale electrolysis was performed with the flux composition 45 wt% MgF2–55 wt% CaF2 with 6 wt% CaO, 4 wt% YF3, and 3 wt% Al2O3 at 1473 K. Al was produced on the TiB2 cathode and oxygen was produced at the inert anode. The YSZ membrane was stable after the electrolysis. The Al product was characterized with SEM and EDS. It was found that there was 6 wt% Mg in the Al, likely due to cathodic concentration polarization. Based on the electrochemical characterization of the cell, an equivalent circuit of the SOM process for Al production is presented. A polarization model for Al and O2 production was developed to analyze polarization losses in the cell according to the equivalent circuit. The modeling results suggested that the performance of the SOM cell can be improved by
lowering the ohmic resistance, the charge transfer resistance and the cathodic concentration polarization resistance; most dominant in our system was the ohmic polarization resistance. Several approaches are proposed to reduce these polarization losses.

Acknowledgments

This research is based on work supported by the Department of Energy through ARPA-E METALS program. The authors thank Alexander Kithes, for assisting the experiments and Dr. Adam Powell of Infinium Inc., Natick MA, for helpful discussions.

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