STABILITY OF YTTRIA STABILIZED ZIRCONIA MEMBRANE IN MOLTEN CaCl₂-CaO MELT

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Abstract

Yttria stabilized zirconia (YSZ), as an excellent oxygen ion conductor, is increasingly used as an oxygen ion membrane for the anode in the FFC Cambridge process. However, using a membrane implies that it exhibits long term stability in the bath. It has been reported that YSZ is stable chemically, but fails electrochemically in molten CaCl₂-CaO. In this work, we report, as opposed to previous reports, that YSZ is chemically not stable in molten CaCl₂-CaO melts. Electromigration only accelerates the instability. The degradation is seen to occur by leaching of yttria in solution leading to the formation of monoclinic zirconia which, being porous, reacts with the molten electrolyte to form calcium zirconate. We will also highlight possible countermeasures.

Keywords: oxygen membrane, degradation, electromigration

1. Introduction

The molten salt electro-deoxidation method popularly known as the Fray Farthing Chen (FFC) Cambridge process is an electrochemical process for the production of metals and alloys directly from their solid oxides by molten salt electrolysis. The process uses solid metal oxide as a cathode in a high-temperature (950 °C-1000 °C) cell with molten calcium chloride/ molten calcium chloride-calcium oxide [1-3] as the electrolyte. This method has been successful in the production of a variety of metals, alloys and intermetallics [4]. The process has even been adapted for the production of titanium on a commercial scale [4]. In the FFC process, the anode material is graphite [2, 5]. The use of graphite causes process and environmental related issues [1, 4, 6]. It results in the generation of gases like CO₂ and CO, as well as potent greenhouse gases like CCl₄, C₂Cl₆ [4, 7, 8]. The CO₂ may dissolve in the melt and may react at the cathode contaminating the metallic product by the reactions below.

\[
\begin{align*}
\text{CO}_2 + \text{O}^{2-} &= \text{CO}_3^{2-} \hspace{1cm} \text{(in melt)} \hspace{1cm} (1) \\
\text{CO}_3^{2-} + 4\text{e}^- &= 3\text{O}^{2-} + \text{C} \hspace{1cm} \text{(at cathode)} \hspace{1cm} (2)
\end{align*}
\]

The formation of carbon by reaction (2) may also cause short circuiting of the cell. The use of inert anodes would thus solve the above problems to a large extent [4, 8]. However, finding a suitable inert high-temperature anode is not a simple task [8]. Ferro et al. [9] in 1998 proposed the use of an oxygen conducting ceramic membrane for the anode during the electrolysis of a CaO-CaCl₂ melt producing calcium metal [9]. The concept was further developed as a solid oxide membrane (SOM) process at Boston University [10, 11]. The SOM process uses an yttria stabilized zirconia tube as a membrane around the anode [10]. Under the applied voltage, the metal oxide that is dissolved in the electrolyte forms a metal
at the cathode and oxygen ions are transported through the membrane to the anode where oxygen gas is released [10, 12]. The concept of using a solid oxide membrane (SOM) has been recently demonstrated in the FFC Cambridge process [13-15].

For a successful (SOM) FFC process, the stability of yttria stabilized zirconia in molten CaCl$_2$-CaO melt is a critical issue. Martin et al. [16] studied the stability of yttria stabilized zirconia in molten CaCl$_2$-CaO melt at 850 °C for 10 h and reported [16] that the membrane is quite stable in a static melt but fails when current is passed through it. The damage was attributed to the leaching of yttria from yttria stabilized zirconia in molten salt by reaction (3) thereby causing transformation of cubic ZrO$_2$ to monoclinic ZrO$_2$ in the membrane, which leads to its cracking

$$Y_2O_3 + O^{2-} = 2YO_2^{-} \quad (3)$$

In a static melt, it was argued that the high solubility of CaO in CaCl$_2$ ensures formation of complex ions like $[\text{Ca}_x\text{OCI}_{2x}]^{2-}$, which decreases the free $O^{2-}$ ions in the molten salt. Though no other studies have been done on the stability of yttria stabilized zirconia in CaCl$_2$-CaO melt, the previous reports of hot corrosion of yttria stabilized zirconia in molten salts like sodium vanadate, sodium sulfate, CaF$_2$-MgF$_2$ etc [17-19], show that damage there is mostly due to the chemical leaching of yttria in static melts. As there is ambiguity on the report of stability of yttria stabilized zirconia in CaO-CaCl$_2$ melts [16] vis-à-vis other molten salts [17-19], the objective of the paper was to reinvestigate the behavior of fully yttria-stabilized zirconia (YSZ- 8 mol%) in a molten calcium chloride, and calcium oxide-calcium chloride melts in a temperature range between 950–1000 °C.

2. Experimental

2.1 Materials

Nano YSZ- 8 mol% (99.99% pure, Tosoh Corporation) powders were used. Cold isostatically pressed pellets and tubes were sintered at 1550 °C to obtain densities >99%. Anhydrous calcium chloride (95% pure, Acros organics) was used. In some experiments, CaO (97% pure, Acros Organics) and yttrium oxide (99.9 % pure, Acros Organics) were also added. The powders were intimately mixed with mortar and pestle. The salts were dried in an oven at 300 °C for 20 h prior to use.

2.2 Compatibility experiments

For the chemical compatibility experiment, around 4 g of dehydrated salts was first added in a quartz cup (15 mm dia, 25 mm height). The pellets were put slowly inside the calcium chloride powders. The quartz cup was then heated at 1000 °C in air and maintained at that temperature for 16 h. All the reacted pellets were then cut in half using a diamond saw and cold mounted in epoxy resin to study the cutting edge.

An electrochemical setup was made to test the electrochemical compatibility of the samples. YSZ- 8 mol% tube (30 mm length) was used as the membrane while the anode was a Kanthal (Fe-Cr-Al) wire (φ of 1 mm) dipped in a silver-alloy paste (melting point 810 °C). A Kanthal coil served both as the cathode and as the pseudo-reference electrode. The salt was heated up to 980 °C and equilibrated for 1 h. The molten salt (CaCl$_2$- 2 wt% CaO) served as the electrolyte. Potentiostatic experiments were performed for 6 h in air using a EG&G 273 potentiostat. The experiments were done by applying a constant voltage of 1.5 V.
section of the tube (portion dipped in the electrolyte) was then sectioned using a diamond saw and the sectioned surface was cold mounted in epoxy resin.

2.3 Characterization of the samples
The samples were analyzed using X-ray diffraction (XRD) (Seifert 3003) from 10° to 80° at a rate of 0.02°/s to determine the phase composition. The cold mounted samples (pellets and tubes) were polished with 1 μm diamond paste. The as-polished samples were then carbon coated and subjected to full quantitative microchemical analysis in an electron probe microanalyzer (JEOL JXA8530F) using wavelength dispersive spectrometry. To determine the extent of the damage at the interface, secondary electron/backscattered electron images of some samples were also taken in a scanning electron microscope (XL30 FEG). The images at the interface showed the degradation behavior clearly.

3. Results and discussions

3.1 Chemical interactions
The XRD of YSZ-8 mol% pellets after chemical interaction with molten salt is shown in Fig 1. Unreacted YSZ-8 mol% is also shown for comparison. It is easy to see that the monoclinic zirconia phase formed in the reacted samples. When the sample was treated in molten CaCl₂-2 wt % of CaO salt, the XRD of the surface (Fig 1 (c)) shows only peaks of calcium zirconate and cubic zirconia. No peak of monoclinic zirconia could be seen. This indicates that the monoclinic zirconia formed due to depletion of yttria at the interface eventually reacts with CaO by reaction (4).

\[
\text{CaO (s) + ZrO}_2 \text{ (s) = CaZrO}_3 \text{(s) (}\Delta G^0 = -35.38 \text{ kJ at 900 °C)})
\]

Even fully dried calcium chloride contains small amounts of calcium oxide, which is why small peaks of the calcium zirconate phase are seen in Fig 1 (b).

Fig 1: XRD of YSZ-8 mol% (a) Before interaction (b) After interaction in molten CaCl₂ for 16 h (c) After interaction in molten CaCl₂-2 wt% CaO for 16 h
Fig 2 shows the elemental mapping of the pellet reacted in molten CaCl$_2$. A line profile is also superimposed in the mapping to indicate the relative concentration across the cross-section of sample/epoxy interface. In Fig 2, the sample is at the left and epoxy is at the right. It can be seen in Fig 2 that there is a clear depletion of yttria at the interface (up to around 15 µm from the interface) and that calcium is present in the same region where yttria is depleted. The formation of CaZrO$_3$ from CaO and ZrO$_2$ starts at a temperature of around 900 °C and is accompanied by a volume increase [20]. At temperatures above 900 °C, the propensity of formation of CaZrO$_3$ is higher. Hence YSZ-8 mol% exposed to salts containing more CaO at higher temperatures will undergo more damage due to the formation of CaZrO$_3$. The pores also showed chlorine peaks (Fig 2) which indicated that the molten electrolyte infiltrates the pores and was retained there.

Fig 2: Elemental mapping of YSZ- 8 mol% reacted in molten CaCl$_2$ at 1000 °C for 16 h

3.2 Electrochemical interactions

The sectioned YSZ-8 mol% tube, after current was passed through it for 6 h, is shown in Fig 3(a). It can be clearly seen that small pores developed across the entire thickness of the tube. The elemental mapping at these pores showed the presence of calcium (Fig 3(b)). The current in YSZ-8 mol% is due to the movement of oxygen ions. Locally, yttria interacted with oxygen ions by reaction (3) and was leached out. This led to the development of a porous monoclinic zirconia phase in these locations. These pores formed a narrow channel, which
allowed the molten salt to infiltrate, and the CaO in the molten salt eventually reacted with the monoclinic zirconia to form calcium zirconate. Therefore, electrochemically, it was seen that the leaching of yttria no longer occurred at the interface but was more localized and spanned the entire thickness of tube. The observation that the membrane fails only electrochemically as reported by Martin et al. [16] may be attributed to the development of the calcium zirconate across the thickness of the tube.

Fig 3: YSZ-8 mol% tube reacted in CaCl$_2$-2 wt% CaO at 980 °C for 6 h after applying voltage of 1.5 V across the Kanthal anode dipped inside the YSZ-8 mol% tube wrt to the pseudo-reference electrode dipped in the electrolyte (a) BSE image and (b) calcium mapping

3.3 Countermeasures

In order to halt the degradation process, 1 wt%, 2 wt% and 5 wt% Yttria was added to the molten CaCl$_2$. The samples of YSZ-8 mol% after exposure to such salts were analyzed by XRD (Fig 4). It can be seen that with all additions of yttria, the monoclinic phase could no longer be detected on the surface of YSZ-8 mol% (when compared to Fig 1(b)). As small amounts of monoclinic phase could be missed by XRD, the interfaces of the same samples were also studied under SEM and EDS. It was verified that the samples exposed to molten CaCl$_2$ containing more than 2 wt% yttria was relatively smooth, with a negligible development of the monoclinic porous phase. To illustrate this, the microstructure of YSZ-8 mol% interface exposed to CaCl$_2$- 2 wt% CaO without and with addition of 5 wt% of yttria is shown in Fig 5(a) and (b). Fig 5 (a) shows that the interface had badly corroded and contains a large amount of pores (up to a region of 100 μm), whereas the same interface was relatively smooth when reacted in a salt containing 5 wt% of yttria (Fig 5(b)). Yttria essentially balances the chemical potential gradient of yttria in salt and stabilized zirconia, thereby
preventing the leaching of yttria from the membrane. The addition of yttria was also seen to prevent the electrochemical degradation of the membranes.

![XRD of YSZ-8 mol% in molten CaCl₂ at 1000 °C for 16 h](image)

**Fig 4**: XRD of YSZ-8 mol% in molten CaCl₂ at 1000 °C for 16 h (a) 1 wt% yttria (b) 2 wt% yttria (c) 5 wt% yttria

![Secondary images of YSZ-8 mol% in CaCl₂-2 wt% CaO](image)

**Fig 5**: (a) Secondary images of YSZ-8 mol% in CaCl₂-2 wt% CaO (b) Secondary images of YSZ-8 mol% in CaCl₂-2 wt% CaO-5 wt% Y₂O₃

4. **Conclusions**

The study shows chemical leaching of yttria occurs in YSZ when put in molten calcium chloride and molten calcium chloride- calcium oxide melts for conditions that correspond to its use in a modified FFC process. Cubic zirconia (in YSZ-8 mol%) transforms to monoclinic zirconia on reacting with molten calcium chloride. There is a formation of a porous zone due to monoclinic zirconia formation. Calcium oxide (present inherently in
calcium chloride or added separately) reacts with monoclinic zirconia to form calcium zirconate. In the electrochemical experiment, local leaching of yttria occurs resulting in the development of calcium zirconate throughout the entire thickness of the YSZ- 8 mol% tube. Addition of yttria to a calcium chloride or a calcium chloride-calcium oxide solution is seen to prevent both chemical and electrochemical leaching of yttria from YSZ.

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