



Corrosion testing of zirconia, beryllia and magnesia ceramics in molten alkali metal carbonates at 900 °C



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HIGHLIGHTS

- Stability of zirconia, beryllia and magnesia in molten carbonates at 900 °C was examined.
- Conclusions were based on XPS analysis of the melt after up to 33 h of exposure.
- Mg showed no signs of degradation in Li₂CO₃–Li₂O and (Li,Na,K) carbonate eutectic melts.
- Beryllia and zirconia showed detectable corrosion.
- Magnesia is a suitable insulator for electrolysis cells containing a Li₂CO₃–Li₂O melt.

ARTICLE INFO

Article history:

Received 10 July 2015

Received in revised form

28 September 2015

Accepted 29 September 2015

Keywords:

CO₂ electrolysis
Molten carbonates
Magnesia
Zirconia
Beryllia

ABSTRACT

An electrochemical cell containing molten Li₂CO₃–Li₂O at 900 °C has been proposed for the conversion of the greenhouse gas CO₂ to CO for chemical energy storage. In the current work, we have examined the corrosion resistance of zirconia, beryllia and magnesia ceramics at 900 °C in the Li₂CO₃–Li₂O and Li–Na–K carbonate eutectic mixtures to identify suitable electrically insulating materials. Conclusions regarding material stability were based on elemental analysis of the melt, primarily via X-ray photoelectron spectroscopy, a particularly sensitive technique. It was found that magnesia is completely stable for at least 33 h in a Li₂CO₃–Li₂O melt, while a combined lithium titanate/lithium zirconate layer forms on the zirconia ceramic as detected by XRD. Under the same melt conditions, beryllia shows considerable leaching into solution. In a Li–Na–K carbonate eutectic mixture containing 10.2 mol% oxide at 900 °C under standard atmospheric conditions, magnesia showed no signs of degradation. Stabilization of the zirconia content of the eutectic mixture at 0.01–0.02 at% after 2 h is explained by the formation of a lithium zirconate coating on the ceramic. On the basis of these results, we conclude that only magnesia can be satisfactorily used as an insulating material in electrolysis cells containing Li₂CO₃–Li₂O melts.

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1. Introduction

Electrochemical reduction of CO₂ to CO is one of the very attractive routes for converting electrical energy from renewable sources into fuel, which may be stored for later use [1–4]. CO can be used in any standard gas turbine to generate electricity, or it can be converted into methanol via a well-established chemical pathway. The technique for CO₂ to CO conversion that we recently described is based on the electrolysis of molten Li₂CO₃ at 900 °C using a Ti

cathode and a graphite or Ti\TiC [5–7] anode. Upon melting, Li₂CO₃ converts to a Li₂CO₃/Li₂O mixture, in which the content of Li₂O (up to 18 at %) is controlled by the pressure of CO₂ in the environment [7]. Electrode reactions in carbonates are in general complex and multi-stage [8–12]. The material-charge balance of the cathode reaction during the electrolysis of molten Li₂CO₃ at 900 °C with a Ti cathode is [6]:



The mechanism of the anode reaction has not yet been identified: neither anode material, graphite or Ti\TiC, degrades during electrolysis and the overpotential does not exceed a few tens of mV

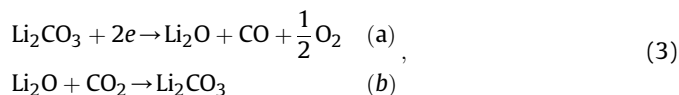
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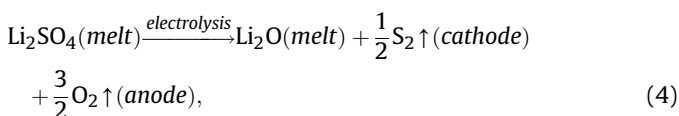
even for very large current densities ($>1.5 \text{ A/cm}^2$) [5]. The material-charge balance of the anode reaction is:



The reaction $\text{CO}_3^{2-} - 2e \rightarrow \text{CO}_2 \uparrow + \frac{1}{2} \text{O}_2$ apparently does not take place because no CO_2 was found in the anode gases even when the concentration of Li_2O is only $\sim 2 \text{ at\%}$ [6]. Thus, a Li_2CO_3 electrolysis cell operates via the self-replenishing cycle:



The electrochemical conversion of CO_2 to CO via electrolysis of molten Li_2CO_3 has a number of advantages compared to alternative CO_2 reduction pathways [6,7]. **(i)** High thermodynamic efficiency (the ratio of the energy supplied with respect to the energy used to drive the reaction) is not uncommon for electrolysis with gaseous products. The entropy term $T\Delta S$ is positive, thereby reducing the decomposition potential below that of the isothermal point: the decomposition potential of Li_2CO_3 is 0.87 V at $900 \text{ }^\circ\text{C}$, which is approximately 30% lower than the isothermal voltage (1.28 V at $900 \text{ }^\circ\text{C}$) ($\Delta G = 246 \text{ kJ/mol}$). This implies that a significant fraction of the heat of reaction can be converted to chemical energy, thereby compensating for ohmic losses. Thermodynamic efficiency close to 100% may result. **(ii)** Since the $\text{Li}_2\text{CO}_3/\text{Li}_2\text{O}$ melt is free of precipitate at $900 \text{ }^\circ\text{C}$ in the presence of $\sim 2 \text{ at\% CO}_2$ [7], dilute sources of CO_2 can be used. **(iii)** The CO_2 to CO conversion is not affected by the presence of water in the incoming gas. **(iv)** Noble metals and solid electrolytes are not required, only welded Ti; therefore, process scale-up is more economically achieved than with a number of other technologies. **(v)** The electrolysis products are physically separated from each other, both within the cell and upon outflow. **(vi)** The method is tolerant to the presence of sulfur in the incoming gas: any sulfur entering the system is eventually converted into sulfate and then removed by electrolysis [13]:



Consequently, sulfur-containing flue gas from power stations can be used as the source of CO_2 .

However, despite all these advantages, the CO_2 to CO conversion by electrolysis of molten Li_2CO_3 faces problems of material compatibility. Electrolysis proceeds efficiently only between 850 and $900 \text{ }^\circ\text{C}$, and at these temperatures, the $\text{Li}_2\text{CO}_3/\text{Li}_2\text{O}$ melt is very corrosive (e.g., it dissolves alumina, Pt and Au) [6,14]. Although the melt is readily contained in a welded Ti container [13], practical application requires construction of multi-cell devices in which insulating materials would play a dual role: (i) for the construction of high-temperature, feed-through electrical connectors and (ii) for the construction of bipolar electrodes (one surface anodic, the other surface, cathodic). Bipolar electrodes are the most common solution for connecting cells in series in order to reach the required voltage. In this way, improved matching to power sources may be accomplished. High melting point ceramics are obvious candidates and in the present study, we report the results of static corrosion testing of zirconia, beryllia, and magnesia ceramics in molten $\text{Li}_2\text{CO}_3/\text{Li}_2\text{O}$.

2. Experimental

Ceramics were obtained from the following sources: partially

yttria-stabilized zirconia (YSZ) from Retsch GmbH (5.2% Y_2O_3 , other oxides $< 0.3\%$, $\sim 1 \text{ at\% Hf}$); beryllia (99.5 at%) and magnesia ($>99.9 \text{ at\%}$) both from The Institute of High Temperature Electrochemistry of the Ural Branch of the Russian Academy of Science. Of these, beryllia is the most costly and zirconia, the least costly. Beryllia and magnesia were in the form of thin, ceramic plates with a total surface area of $100\text{--}120 \text{ mm}^2$ while the partially yttria-stabilized zirconia sample had the approximate shape of a short spherocylinder with diameter $\sim 12 \text{ mm}$, length $\sim 9 \text{ mm}$ and surface area $550\text{--}600 \text{ mm}^2$. The crystal structure of the pristine zirconia sample is tetragonal; following immersion in the melt, a phase transition to monoclinic takes place. The cooled sample displays bi-phasic behavior, characteristic of weakly doped ZrO_2 . The ceramic samples were immersed in $100 (\pm 5\%) \text{ cm}^3$ of the Li_2CO_3 melt (Acros Organics), or of a Li–K–Na carbonate eutectic, in a titanium container for 2–33 h at $900 \text{ }^\circ\text{C}$. For preparation of the eutectic, Na_2CO_3 and K_2CO_3 were obtained from Alfa Aesar. Prior to the immersion of the ceramics, it was verified that the melt did not contain detectable amounts of Mg, Zr or Be. Mg may pose a particularly serious problem as some commercially available sources of Li_2CO_3 contain $0.5\text{--}100 \text{ mg/kg}$ of Mg (depending on the purity [15]). Upon heating, Li_2CO_3 converts to a $\text{Li}_2\text{CO}_3/\text{Li}_2\text{O}$ mixture releasing CO_2 . In 1 atm CO_2 the concentration of Li_2O in the $\text{Li}_2\text{CO}_3/\text{Li}_2\text{O}$ mixture is $\approx 0.2 \text{ mol\%}$ [7]; in air, the concentration of Li_2O reaches $\approx 18 \text{ mol\%}$. Probes ($0.1\text{--}0.4 \text{ cm}^3$) of the melt were taken using a cold rod and their content analyzed by energy-dispersive X-ray spectroscopy (EDS, qualitative analysis) and X-ray photoelectron spectroscopy (XPS, quantitative analysis) to determine the elemental composition. We found experimentally that this approach is far more sensitive than measuring weight loss after separating the ceramics from the solidified melt. EDS measurements were made on a Leo-Supra scanning electron microscope (SEM). XPS measurements of the Li(1s), C(1s), O(1s), Na(1s), K(2p), Mg(1s), Be(1s) and Zr(3d) core levels were carried out with the Kratos AXIS ULTRA XPS system using a monochromatic Al K_α X-ray source ($h\nu = 1486.6 \text{ eV}$) at 75 W and detection pass energies ranging between 20 and 80 eV . A low-energy electron flood gun (eFG) was applied for charge neutralization. Depending on the shape of the background, either a linear or Shirley background [16] was used to extract the surface concentrations of the different elements. Curve fitting analysis was based on background subtraction and use of mixed Gaussian–Lorentzian line shapes [17,18]. Powder X-ray diffraction (XRD) patterns were measured on a Rigaku TTRAXIII theta–theta diffractometer at grazing incidence (fixed angle 4.5°) with Cu K_α radiation. Phase identification and quantitative analysis were performed with Jade 9 (MDI, CA) with reference to the Powder Diffraction File (PDF-ICDD) and the Inorganic Crystal Structure Database (FIZ Karlsruhe). X-ray fluorescence (XRF) was measured on a benchtop XRF ED instrument (model EX-Calibur, Xenometrix, Migdal Haemek, Israel).

3. Results and discussion

3.1. Ceramic stability in molten $\text{Li}_2\text{CO}_3/\text{Li}_2\text{O}$

Fig. 1 (red (lower) trace) shows the X-ray photoelectron spectroscopy (XPS) measurement of a cold rod probe of the $\text{Li}_2\text{CO}_3 + 0.2 \text{ mol\% Li}_2\text{O}$ melt taken after a YSZ ($T_{\text{mp}} = 2715 \text{ }^\circ\text{C}$) ceramic spherocylinder had been immersed for 9 hrs at $900 \text{ }^\circ\text{C}$ under 1 atm of CO_2 . The 3d photoelectron peaks of Zr, if present, would appear at 182.5 eV ($5/2$) and 184.9 eV ($3/2$). It is clear that the spectrum shows no evidence of transfer to the melt of any detectable amount of Zr. Similar negative results were obtained when the YSZ sample had been in the melt for up to 33 h (data not shown). However, power station flue gas, the intended source of

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