



Influence of mass transfer and electrolyte composition on anodic oxygen evolution in molten oxides



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ARTICLE INFO

Article history:

Received 27 April 2016

Received in revised form 11 September 2016

Accepted 26 September 2016

Available online 28 September 2016

Keywords:

molten oxides
oxygen evolution
rotating electrode
ac voltammetry
iridium
silicates

ABSTRACT

The electrochemistry of anodic oxygen evolution on iridium in silicate-containing molten oxides at 1570 °C was experimentally investigated using both direct and alternating current methods. Static and rotating electrode results show the presence of anodic reactions of iridium in addition to oxygen evolution. In the context of electrochemical engineering of molten oxide electrolysis, the results confirm prior theoretical calculations (Allanore, 2013) that suggested an essential role of convection and electrolyte composition on the ability to sustain oxygen evolution at high current densities. In addition, the reported results show that electrochemical measurements in molten oxides coupled with mass-transfer models are complementary characterization tools for oxygen chemistry.

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1. Introduction

Molten oxides are one possible electrolyte for the direct decomposition of metal oxide to produce metal and oxygen in an electrochemical process. Assuming the dissociation of the feed oxide MO into its constituent ions in the molten oxide electrolyte, the target cathode and anode reactions are commonly written as:



As discussed in a recent review [1], numerous examples of successful production of metal by electrolysis in molten oxides have been reported (e.g. for Fe, Mn, Si) but knowledge of the underlying electrochemistry is limited. In particular, insights into the anodic reaction (2) are lacking, and fields such as geology, glass science, metallurgy and nuclear processes may greatly benefit from additional insight into oxygen chemistry in molten oxides. According to prior electrochemical investigations, reviewed in references [1] and [2], the free oxide ion (O^{2-}) is the reacting species at the anode. Prior work [2] proposed to integrate available

literature data and knowledge of the physical chemistry of oxygen in molten oxides to evaluate the possible mass-transfer limitations on the oxygen evolution reaction (2). In that prior electrochemical engineering approach, the role of convection induced by gas evolution was put forth as an important phenomenon that enhances the limiting current for oxygen evolution in molten oxides.

The present work aims to provide experimental evidence of the role of mass-transfer on reaction (2), herein conducted on an iridium anode. Electrochemical measurements of the anodic evolution of oxygen on iridium as both a static and a rotating electrode, using direct (dc) and alternating (ac) current methods, are reported herein. In addition, electrochemical measurements in different electrolytes are presented, demonstrating the utility of electrochemistry for probing oxygen chemistry *in-situ*. Lastly, the essential role of the supporting electrolyte design for the evolution of oxygen by electrolysis in molten oxides is highlighted.

2. Experimental

2.1. Materials

Reagent grade (purity min. 98%) silica, alumina, magnesia, and calcia powders were individually weighed and manually mixed by shaking in a polyethylene bottle prior to being packed directly in an alumina crucible (purity min. 98%). Table 1 provides a list of the compositions investigated and their calculated optical basicity, along with their density and dynamic viscosity reported in

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Table 1

Composition and physical-chemical properties of the electrolytes at 1600 °C.

ID	Composition wt %					Optical basicity	Density kg m ⁻³	Kinematic viscosity m ² s ⁻¹
	CaO	MgO	Al ₂ O ₃	SiO ₂	Fe ₃ O ₄			
SA1	27	8	23	42	–	0.62	2720	3.62 × 10 ⁻⁴
SB2	31	8	17	44	–	0.63	2705	2.75 × 10 ⁻⁴
SB2F	30.3	7.8	16.6	43.1	1.9	–	–	–
SB3	37	10	19	34	–	0.66	2749	1.47 × 10 ⁻⁴
SB4	50	6	0	44	–	0.68	2651	7.92 × 10 ⁻⁴

reference [3]. Only one electrolyte contained magnetite (purity min 98%), added at around 2 wt %.

Iridium (>99.9%, Furuya Metals, Japan) was used as an anode in the form of a wire (0.5 mm diameter) or a rod (3 mm diameter). Molybdenum (Ed Fagan, USA) was used as a quasi-reference (rod of 3 mm diameter) and counter electrode (rod of 3 mm diameter or foil of 0.5 mm thickness shaped into a cylinder occupying the circumference of the crucible section), welded to molybdenum rods (3 mm) that served as current leads. With this study being dedicated to anodic oxygen evolution, the counter electrodes are cathodes (see [1]). The corresponding cathode reactions in the presence of iron are either Fe³⁺ reduction to Fe²⁺ or Fe²⁺ reduction to Fe⁰ that alloys with molybdenum. In the electrolytes free of iron, the cathode reaction is the reduction of silicon, which also alloys with molybdenum. With the exception of the rotating cylinder electrode, electrode leads were protected using alumina tubes (6.4 mm diameter, CoorsTek), and alumina cement was used to cover the welds exposed to high temperature (Alumina Cement Type AL-CEM, Zircar). Viton™ O-rings and epoxy were used to seal the tubes and the furnace cap from the ambient environment. All experiments were conducted in argon atmosphere with a flow rate of 150 mL min⁻¹ (Airgas, <10 ppm O₂), leading to an oxygen partial pressure in the tube furnace atmosphere of 50 ppm measured at the outlet.

2.2. High Temperature Assembly

The alumina crucible (600 cm³ capacity, internal diameter of 6.5 cm) containing the electrolyte (around 150 cm³ or 4 cm height when molten) was placed in a secondary crucible, itself placed in a closed one end alumina tube equipped with a water-cooled cap with Ultra-Torr™ vacuum feed-through fittings for the movement and insertion of the electrode leads. The whole assembly was placed in a furnace equipped with lanthanum chromite heating elements (model: PVT 18/100/350, Carbolite, UK). The furnace temperature controller was set at a temperature of 1630 °C, with a ramping rate of 84 °C h⁻¹. Independent measurement of the temperature directly above the electrolyte with a B-type thermocouple confirmed a 60 °C difference with the furnace set-point temperature. The reported temperature in this work is therefore 1570 °C.

2.3. Electrode Configuration

The electrode configuration for the static anode measurements consisted of three vertical electrodes in a triangular configuration as viewed from above the crucible. The working electrode was an iridium wire with an exposed surface area ranging from 0.017 cm² to 0.10 cm² depending on the immersion depth. The two other electrodes, counter and reference, were made of molybdenum rods immersed at least 1 cm deeper than the tip of the iridium working electrode.

The rotating iridium electrode (see Appendix A for a schematic) consisted of a 3 mm diameter iridium rod inserted in a

molybdenum rotating shaft (1 cm outer diameter OD) to leave around 1 cm of iridium exposed. The shaft was guided by a molybdenum tube (2.54 cm OD) and a stabilization ring. The molybdenum tube and the shaft were able to jointly slide along the length of the tube furnace through the cap via a vacuum fitting (2.54 cm ID). The seal between the rotating shaft and the tube was maintained outside of the furnace by a custom-made aluminium casing and compression cap, equipped with a conical spring seal (Vulcan Type 8). Rotation of the shaft was achieved through an overhead stirrer (Heidolph 2102 RZR) equipped with a rubber coupling. Electrical connection was made by connecting a wire between the shaft and an aluminium tube extending through and above the stirrer chuck. The aluminium extension tube was then connected to a rotary electrical contact (Mercotac, Model 105). The counter electrode for the rotating electrode experiments was a molybdenum cylinder that occupied the internal circumference of the alumina crucible.

For all measurements, after a holding time at the target temperature of half an hour to one hour, the reference and counter electrodes were successively lowered into the molten electrolyte. The melt position was detected through a sharp decrease in the resistance between the electrodes as measured with an ohmmeter. With the two electrodes in position, the working electrode was lowered last and its contact with the melt determined by the ohmmeter. The working electrode was then immersed between 2 mm and 5 mm into the electrolyte.

2.4. Electrochemical Measurements

Electrochemical signals from the static electrode were recorded with a potentiostat (model 1287, Solartron) and a frequency response analyzer (FRA) (model 1260, Solartron). Measurements from the rotating electrode were recorded using another potentiostat/FRA (PGSTAT302N, AutoLab). The open-circuit potential (OCP) was recorded after immersion of the electrodes, typically followed by electrochemical impedance spectroscopy (EIS) at the open-circuit potential. This last measurement was used post-experiment to evaluate the uncompensated resistance, obtained as the real component of the impedance when the imaginary component is zero. The potentials reported in this work are corrected by the ohmic drop arising from the uncompensated resistance and referenced to the molybdenum reference electrode potential. The molybdenum electrode is assumed to be in equilibrium with MoO₂(s).¹ The reference potential is then assumed to be fixed by the equilibrium reaction (3), for which the standard decomposition potential difference at 1570 °C is

¹ The choice of MoO₂(s) as the solid oxide species in equilibrium with Mo is inherited from the Mo–O₂ phase diagram which indicates this solid oxide as the stable species at 1600 °C in a reducing atmosphere. The underlying calculations are obtained from Factsage 7.0, see reference [4] for the corresponding method.

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