

Review article

Electrochemical engineering of anodic oxygen evolution in molten oxides

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ABSTRACT

Molten oxide electrolysis (MOE) is a metal extraction process that exhibits an exceptionally high productivity in comparison with other electrowinning techniques. Furthermore, MOE has the ability to generate oxygen as an environmentally benign byproduct, which is a key asset to improve metal extraction sustainability. From an electrochemical engineering standpoint, the high concentration of metal cations dissolved in the electrolyte justifies cathode current densities above $10,000 \text{ A m}^{-2}$. At the anode, the available data suggest a mechanism of oxidation of the free oxide anions which concentration in oxide melts is reported to be limited. In this context, the application of available mass-transfer correlations for the anodic oxygen evolution suggests a key role of convection induced by gas bubbles evolution.

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1. Introduction

Society environmental awareness, in particular the issue of greenhouse gases emissions, is a strong incitation for the extractive metallurgy sector to reconsider its core processes. Metals and mining industries were indeed among the largest industrial GHG emitters in 2010 in the USA [1]. In this context, electrolytic techniques have been put forward for example by the steel industry as

a mean to take benefit of future 'decarbonated' electricity. Among innovative electrochemical processes, molten oxide electrolysis (MOE) is the only concept that enables the direct reduction of oxide feedstock to liquid metal, a key asset for high-throughput metal production. The concept relies on the ability of a mixture of molten oxides – hereafter designated as melts or electrolyte – to dissolve significant amount of the oxide feedstock of interest and operate at a temperature higher than the targeted metal melting point. This technique has been investigated for the production of ferromanganese [2] or titanium [3]. One of the recent development of MOE is for iron, which has been produced in the liquid phase [4] along with oxygen gas [5] at current densities higher than 10000 A m^{-2} in laboratory-scale cells. Such exceptional current densities are key to

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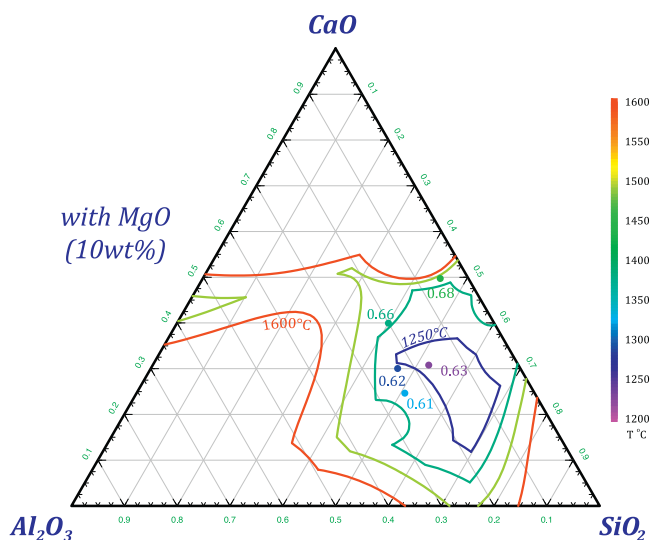


Fig. 1. Liquidus projections from 1250 to 1600°C for the quaternary system calcia–silica–alumina–magnesia (10 wt%). Dots represent some of the compositions of interest for MOE, the numbers indicate their corresponding optical basicity.

lower the footprint of the foreseen industrial scale process, but also raise interesting questions from an electrochemical engineering standpoint.

The net reactions on the cathode (1) and the anode (2) provide a macroscopic description of MOE where M is the targeted metal:



The concentration of metal cations feedstock (M^{n+}) in the electrolyte is high ($C_{\text{bulk}} \sim 3000 \text{ mol m}^{-3}$, see [4]) though the corresponding oxide represent typically less than 10 wt% of the total oxide content. The order of magnitude of metal cation diffusivity is similar to the one observed in aqueous solutions, for example $D_{\text{Fe}^{2+}} \sim 10^{-9} \text{ m}^2 \text{ s}^{-1}$ in melts at 1600°C [6]. The specific value depends on the melt composition and the metal cation valence, but available data suggest that such order of magnitude is of relevance for most cations and melts investigated so far. Assuming a Nernst model of the cathode interface (Nernst layer thickness

of $\delta = 5 \times 10^{-5} \text{ m}$), it is possible to estimate the limiting cathode current density for reaction (1) via:

$$j_{\text{lim}} = nF \frac{D}{\delta} C_{\text{bulk}} \quad (3)$$

In the foreseen conditions the limiting cathode current density is predicted to exceed $10,000 \text{ A m}^{-2}$, in agreement with previous experimental reports [4].

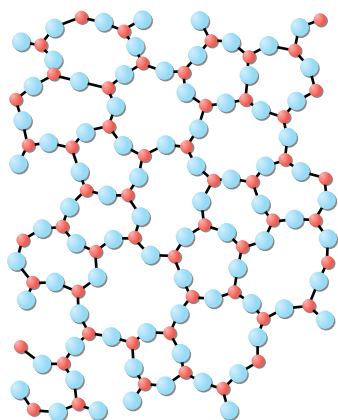
The anodic oxygen evolution reaction (2) requires more careful examination. First, the chemistry of oxygen in molten oxides is unclear and compelling arguments are lacking to establish the exact nature of the reactant. Second, the generation of oxygen gas on the anode is expected to influence the mass transfer conditions and is a topic of interest to a broad community.

In the following, it is proposed to discuss the electrochemical engineering aspect of the oxygen evolution reaction in the molten oxide supporting electrolytes in absence of the metal oxide feedstock. This approach is adopted in order to simplify the electrochemistry of the system, in which the simultaneous presence of several metal cations (e.g. Fe^{3+} and Fe^{2+}) can lead to complications, for example the potential existence of electronic conductivity [7]. The first part provides a review of the physical chemical properties of the candidate electrolyte in the temperature range of iron production by MOE. An overview of oxygen chemistry in oxide melts is also presented. The second part is dedicated to a summary of the literature on oxygen evolution in oxide melts. The last part is a discussion of the possible transfer phenomena that can arise when generating oxygen in such electrolytes, and their influence on the corresponding limiting current density.

2. Properties of molten oxides supporting electrolyte

The design of an electrolyte for MOE is an important task to optimize the energetic efficiency of the electrolysis as well as the stability of the refractory or the anode materials [5]. The supporting electrolyte components are oxides, encompassing: silica (SiO_2), alumina (Al_2O_3), magnesia (MgO) and calcia (CaO). In the recent developments, the concentration of magnesia is fixed at around 10 wt%, so that a ternary diagram is suitable to represent some of the candidate electrolyte compositions (Fig. 1), computed using the software FactSage™ [8]. Four liquidus projections have been plotted to illustrate the broad range of possible compositions and melting points.

a. covalent silica melt (acidic)



b. 'ionic' melt (basic)

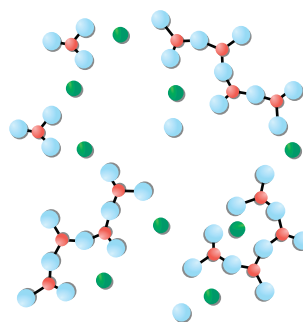


Fig. 2. Schematic structural difference between a pure silica melt (a) and a more basic, ionic melt obtained by addition of a network modifier like calcia (b).

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