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The role of foreign cations in enhancing the oxygen solubility properties of alkali molten carbonate systems: Brief survey of existing data and new research results

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ARTICLE INFO

Article history:

Received 25 November 2013

Received in revised form

5 February 2014

Accepted 7 February 2014

Available online 5 March 2014

Keywords:

Oxygen solubility

Oxygen dissolution mechanisms

Alkali molten carbonates

Rare earth

Alkaline earth

ABSTRACT

This work presents a summary of experimental data on the oxygen solubility-speciation properties of alkali molten carbonates that have been obtained by the authors through the development of a highly sensitive analysis method. The purpose of this summary is to show in particular the effect of foreign cation additions on both oxygen solubility and dissolution mechanisms at 650 °C. Our findings may be used to clearly indicate that rare earth and magnesium cations are the most effective in enabling oxygen solubility and basicity/oxidizing melt properties. The second part of this work reports new experimental results concerning the effect of simultaneous additions of La and Mg cations to an eutectic Li/Na carbonate system. A dramatic increase in oxygen solubility and active peroxide oxygen species has been found, thus revealing a strong synergistic effect of rare earth and alkaline earth cations on the molten carbonate oxygen chemistry. The results of this investigation suggest therefore that foreign cation addition is a potentially attractive option to design alkali molten carbonate salts with a high oxidizing power.

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Introduction

The historical development of alkali molten carbonate research can be traced back to the late fifties at the times of early Molten Carbonate Fuel Cell (MCFC) programmes [1]. Since then, lithium, potassium and sodium carbonates in eutectic composition are dominated the interest as MCFC electrolyte, both in research and industry communities, because carbonate eutectics are low-viscosity liquids at

typical MCFC operating temperatures with minimal Chemla mobility effects and high conductivity properties [2].

Oxygen solubility in alkali molten carbonates is another parameter of importance in MCFC technology. In fact, the solubility of O₂ and CO₂ reactant gases involved in the cathodic electrochemical reaction is a key reaction/mass transport parameter, which affects the oxygen electro-reduction process and the overall MCFC electrochemical performance as well [1]. In this context, there is now a large body of evidence on oxygen solubility mechanisms and factors

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<http://dx.doi.org/10.1016/j.ijhydene.2014.02.042>

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affecting its solubility. Physical O₂ solubility in alkali molten carbonates is usually a negligible dissolution mechanism at temperatures above 600 °C [3]. Absorption and solubilisation of molecular oxygen in molten carbonates is a fast chemical process involving a series of complex reactions with the carbonate ions (CO₃²⁻) and resulting in the formation of highly chemically reactive radical or anionic oxygen-based species like superoxide (O₂⁻) and peroxide ions (O₂²⁻) [4–6]. Their chemical reactivity and oxidizing power are much higher than molecular oxygen, which can be explained on the basis of significantly lower strength of their O–O bond [7]. Several studies have also highlighted that the active oxygen speciation, namely their concentration and relative distribution in the carbonate system is a strong function of acid-base melt properties (see, for example [6]). Thus, on the basis of thermodynamic stability calculations, it can be predicted that highest oxygen solubility values are achievable in conditions of high melt basicity for their capability to dissolve the largest amounts of oxygen in form of stable peroxide anions [6].

In the course of years, one MCFC research area has focused on melt additions of foreign cations such as alkaline-earth and rare-earth cations as effective basicity promoters for adjusting the acid-base melt chemistry in an attempt to minimize performance degradation of electrodes and metallic hardware in direct contact with the corrosive melt [8–11]. In this context, the role of non-alkali cations on the oxygen solubility and its dissolution behaviour has been at the focus of our recent research activity. A preliminary literature survey showed that the oxygen solubility data had been largely collected thoroughly in the sixties and then received a sporadic attention in the decades following [5,12–16]. In spite of its chemical dissolution mechanism, all these solubility works were in good agreement with each other in showing that oxygen solubility in alkali molten carbonates is very low being in the order of some fraction of mol ppm/cm³, at 650 °C. At beginning of our investigations, it was soon realized that past analytical methods reported in literature for the determination of dissolved oxygen at such trace levels were absolutely inadequate for obtaining high precision and accurate data, as it would be indeed required for a robust oxygen speciation analysis. Traditional techniques for estimating oxygen gas solubility in alkali carbonate melts can be classified as in-situ chemical titration or melt quenching measurements. Other methods based on gas solvation by volumetric or manometric devices have been used with little success due to erratic sorption/desorption gas effects [1]. The most extensive measurements were made in the late sixties by Broers and co-workers, who used amperometric titration method of an oxygen-saturated melt by adding stepwise solid Na₂SO₃ as a reducing agent [12]. Standard errors involved either in melt-quenching methods or redox titrimetric methods ranged from 20 to 50%, mainly for the presence of spurious results, which are an inherent problem of most high temperature measurements [1]. Therefore a highly sensitive analytical method was developed for the oxygen assessment in alkali molten carbonates by indirect FAAS (Flame Atomic Absorption Spectrometry) Cr⁶⁺ determination. The precision of the method was better than 10%, whereas the detection limit was as low as 3 × 10⁻³ mol ppm cm⁻³ (calculated as the concentration corresponding to three times the standard deviation of

a blank sample divided by the method analytical sensitivity, i.e. the slope of the calibration curve) [17,18]. Thus, it has been possible to study the effect of foreign cations on the oxygen solubility and its chemical dissolution mechanisms in the most common MCFC electrolytes based on Li/Na and Li/K binary carbonate systems [3,19–23]. It has been found that the additions of small amounts (a few mol %) of rare-earth elements such as La and Gd as well of alkaline-earth elements such as Mg give rise to electrolytes with high oxygen solubility and large amounts of dissolved reactive oxygen species. Unfortunately, foreign cation addition is not a practical and easy-to-use approach in real MCFC systems since most foreign cations strongly inhibit the ionic electrolyte conductivity [24].

However, the fast growing of molten carbonate research areas for non-electrolyte applications as solvents, reaction and destruction media, and catalysts for novel and sustainable industrial processes suggests that oxygen solubility-speciation properties may be of great significance in most of these new sustainability-driven applications, in particular in those where high oxidizing properties are required [25–31]. For instance, there is a recent return of interest for the use of alkali molten carbonates in Molten Salt Oxidation (MSO) processes for disposal of highly toxic, dangerous and even difficult-to-burn organic-containing energetic wastes (i.e., scrap tyres). In order to enable the oxidizing power of molten carbonates, foreign anions like chlorides and sulphates are commonly added with the purpose of slightly increasing the oxygen solubility in the melt [31]. Recent advances in the field have been made by Griffiths and co-workers [32], who have reported that nitrate is much more effective as foreign anion to generate a carbonate melt with a very high oxidizing power. The studies of these authors clearly demonstrate that nitrates added to carbonate melts into small amounts (i.e., 3 wt % KNO₃) will act as effective oxidizing catalysts by allowing the stable formation of high concentrations of superoxide and peroxide anions. Alkali cation composition is known to similarly affect the oxygen solubility, although varying the nature of the alkali cation has only a minor effect on the capability of molten carbonate to chemically absorb gaseous oxygen [3].

On the basis of above-mentioned considerations, we present here a summary of oxygen solubility data gathered in various alkali binary electrolytes containing alkaline-earth and rare-earth elements. In our expectations, this work, which also includes unpublished solubility data, could be particularly useful in the context of new research areas on molten carbonate salts. More in detail, it will be shown that a combined addition of La and Mg cations results in the formation of a carbonate melt with an exceptionally high concentration of dissolved oxygen that could be of interest for MSO applications.

Summary of previously published data

Simply stated, our oxygen solubility-speciation analysis method involves the addition of an excess Cr₂(SO₄)₃ salt as reducing agent to a gas-equilibrated melt sample. The melt samples are withdrawn by quenching method and then dissolved in non-oxidizing HCl acid. The speciation of Cr⁶⁺ is carried out by a well-known complexation reaction with ammonium pyrrolidine dithiocarbamate (APDC), followed by

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