Lux-Flood Basicity of Mixed La$_2$O$_3$-Alkali Molten Carbonates Determined by Analysis of their Oxygen Solubility Properties

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**Abstract:** The Lux-Flood basicity of La$_2$O$_3$-containing alkali molten carbonate mixtures has been quantitatively estimated by a gas solubility method based on the use of acidic gaseous O$_2$ for the titration of the oxide concentration in the melt. The amount of gaseous oxygen dissolved in the melt in form of peroxide ion has been taken as a quantitative probe for the carbonate basicity. Results demonstrate that addition of a 0.5 mol % of La$_2$O$_3$ to alkali carbonates is able to dramatically increase the melt basicity and that the degree of this basicity change mostly depends on the melt composition in terms of the average cation size of the alkali carbonate mixture. Plausible dissolution paths of La$_2$O$_3$ in molten carbonates under both acidic and basic regimes are also discussed.

**Keywords:** Lux-Flood basicity, alkali molten carbonates, lanthanum oxide, oxygen solubility, peroxide concentration, La$_2$O$_3$ dissolution mechanism.

**INTRODUCTION**

In the course of author's recent investigations on the oxygen gas solubility properties of eutectic carbonate melts an accurate analytical method was developed for the determination of the various forms of dissolved oxygen under predetermined O$_2$-CO$_2$ gas mixtures [1]. The analytical method is based on a redox chemical titration of all the active oxygen species present in the melt (molecular oxygen, peroxide, superoxide anions) with the Cr$^{3+}$ added in excess as Cr$_2$(SO$_4$)$_3$ salt. The tiny amounts of Cr$^{6+}$ ions, thus produced, are extracted and concentrated in an organic solvent, from which they can be accurately determined by spectrometric analysis. Due to its high accuracy, the method was proved to be suitable to distinguish the nature and the relative concentrations of the active oxygen species with a linear regression analysis of the solubility data taken at various O$_2$ and CO$_2$ partial pressures.

During such investigations, the solubility of the oxygen gas was found to sharply rise after minor additions of lanthanum and gadolinium oxides (i.e., 0.5 mol %) to the carbonate melts [2]. The results are summarized in Fig. (1) as a function of temperature. It can be noted that with the introduction of rare earth cations oxygen solubilities are subjected to drastic changes at temperatures above 873 K and that the extent of these changes are also affected by the carbonate composition with the highest effects being observed in the lithium-sodium carbonate. It was found that the dissolution of the gaseous oxygen takes place almost exclusively through redox reactions with the melt either to give almost exclusively peroxide anion in the lithium-sodium carbonate or a mixture of superoxide and peroxide anions in the lithium-potassium carbonate (Table 1) [1,2]. Striking was the high peroxide concentration in the lithium-sodium carbonate system indicative that rare earth oxides should have induced the formation of a very strongly basic medium even under relatively high CO$_2$ partial pressures ($P_{CO_2} > 0.2$ atm) in accordance with the known basic character of rare earth oxides. In this respect, it is worth mentioning the intensive research conducted by the Ota’s group [3,4] in these last few years providing a solid basis for the understanding of rare earth effects on molten carbonate properties. In particular, the lower NiO cathode solubility observed in a molten carbonate with added La$_2$O$_3$ was ascribed to an abrupt melt basicity increase [3]. Main intention of this work is therefore to describe the spectacular changes in Lux-Flood basicity of alkali carbonate mixed with rare earth oxides by using a gas solubility method for a quantitative evaluation of these basicity changes. Owing to the lack of precise literature information about rare earth chemistry in molten carbonate salts,

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**Fig. (1).** Oxygen solubility properties expressed as molecular oxygen equivalent in the temperature range 823-923 K for the lithium-sodium (53Li+47Na) and lithium-potassium (62Li+38K) eutectic carbonates with and without addition of 0.5 mol % of Re$_2$O$_3$ (Re = La, Gd).
plausible mechanisms for the rare earth oxide dissolution are also tentatively proposed as a means to explain their strong action on the carbonate basicity. For sake of simplicity, the discussion will be limited to the case of lanthanum, which is the most soluble rare earth element in alkali molten carbonates [4].

**THE GAS SOLUBILITY METHOD TO MEASURE LUX-FLOOD BASICITY**

Basicity is one of the most important properties of oxidic systems (i.e., oxidic glasses, slags and oxo-anion salts) in the molten state. Unlike aqueous systems, an unified acid-base theory does not exist for such oxidic systems. Basicity may be defined invoking different concepts such as thermodynamic oxide ion activity, network modification or electronic polarizability depending on the nature of the chemical bonding in the melt. In oxo-anion salts (i.e., carbonate, nitrate, sulphate salts) the acid-base processes are conveniently described as reactions of detachment or addition of "free" oxide ions according to the theory developed by Lux and Flood [5,6]. On the contrary, in slag and oxidic glass systems, it is rather difficult to define a thermodynamic oxide ion activity as the oxide ion has a strong tendency to interact with metal cations on the basis of electronegativity differences. In these systems the basicity, often termed as optical basicity, is usually expressed in terms of electron donor power of the oxide ion rather than in terms of oxide ion activity.

A variety of methods have been applied in literature to determine basicity such as electromotive force [7], gas solubility [8-10], redox equilibria of transition metal ions [11] and spectroscopic methods [12]. The electromotive force method using galvanic cells is the most employed method to measure Lux-Flood basicity as it is the only available method to determine the thermodynamic oxide ion activity. However, in oxo-anion salts, where only relatively small oxide concentrations exist, the gas solubility method may also provide sufficiently accurate estimations of basicity. The gas solubility method is applicable when there is a chemical interaction between the molten oxide ion and a gas reactant, from which the oxide concentration can be estimated by analysis of the gas consumed in the reaction (i.e., gas solubility). An excellent description of the gas solubility method is given in [13]. The gas solubility is not a general method for Lux-Flood basicity determinations being applicable only to melts containing considerable amounts of oxide ions, i.e., basic melts. In acidic melts, in fact, the solubility of an acidic gas becomes independent from oxide ion concentration being dictated only by its physical solubility in accordance to the well known Henry’s law.

In a basic molten carbonate environment, three elementary Lux-Flood acid-base equilibria involving O2 and CO2 gases can be considered to take place as follows [14]:

\[
\begin{align*}
\text{CO}_2 + \text{O}_2^{2-} & \rightleftharpoons \text{CO}_2^{2-} & K_4 = 0.44, K_{\text{poxo}} = 0.32 \\
0.5\text{O}_2 + \text{O}_2^{2-} & \rightleftharpoons \text{O}_2^{2-} & K_5 = 0.23 \\
0.75\text{O}_2 + 0.5\text{CO}_2^{2-} & \rightleftharpoons \text{O}_2^{2-} + \text{CO}_2 & K_6 = 1.06
\end{align*}
\]

Table 1. Summary of Oxygen Dissolution Mechanisms with the Corresponding Equilibrium Constants Determined in Both Eutectic Lithium-Sodium (53Li+47Na) and Lithium-Potassium (62Li+38K) Carbonates with and without Re2O3 Additives (Re = La, Gd), at 873 and 923 K. Data Collected from Refs. [1] and [2]

<table>
<thead>
<tr>
<th>Melt Composition (mol %)</th>
<th>T / K</th>
<th>O2 Dissolution Mechanism</th>
<th>Apparent Equilibrium Constants (mol ppm cm−3 atm−x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(62Li+38K)</td>
<td>873</td>
<td>molecular</td>
<td>K_4 = 0.157</td>
</tr>
<tr>
<td></td>
<td>923</td>
<td></td>
<td>K_4 = 0.23</td>
</tr>
<tr>
<td>(62Li+38K+0.5La2O3)</td>
<td>873</td>
<td>molecular</td>
<td>K_4 = 0.30</td>
</tr>
<tr>
<td></td>
<td>923</td>
<td></td>
<td>K_4 = 0.16; K_5 = 0.37</td>
</tr>
<tr>
<td>(62Li+38K+0.5Gd2O3)</td>
<td>873</td>
<td>molecular</td>
<td>K_4 = 0.43</td>
</tr>
<tr>
<td></td>
<td>923</td>
<td></td>
<td>K_4 = 0.27; K_5 = 0.25</td>
</tr>
<tr>
<td>(53Li+47Na)</td>
<td>873</td>
<td>superoxide+peroxycarbonate</td>
<td>K_4 = 0.149</td>
</tr>
<tr>
<td></td>
<td>923</td>
<td></td>
<td>K_4 = 0.14; K_{\text{poxo}} = 0.11</td>
</tr>
<tr>
<td>(53Li+47Na+0.5La2O3)</td>
<td>873</td>
<td>peroxide</td>
<td>K_5 = 0.38</td>
</tr>
<tr>
<td></td>
<td>923</td>
<td></td>
<td>K_5 = 1.08</td>
</tr>
<tr>
<td>(53Li+47Na+0.5Gd2O3)</td>
<td>873</td>
<td>peroxide+peroxycarbonate</td>
<td>K_5 = 0.44; K_{\text{poxo}} = 0.32</td>
</tr>
<tr>
<td></td>
<td>923</td>
<td></td>
<td>K_5 = 1.06</td>
</tr>
</tbody>
</table>

*The suffix x depends on the oxygen dissolution mechanism. Its value is -1 for molecular (i.e., physical) dissolution, 0.25 for superoxide; 0.5 for peroxycarbonate and -0.5 for peroxide mechanism, respectively.*
It is important to outline that a pure O\textsubscript{2} gas cannot be used instead of a CO\textsubscript{2} gas as it can be neglected under such conditions. In moderately basic environments, the superoxide amount cannot be neglected as evident from analysis of the following equilibrium, which is obtained as linear combination of eqs. (2)-(3):

\[
2O_2^{2-} + 0.5O_2 = 2O_2^2 + O_2^2
\]  

(6)

This equation shows that the stability of the peroxide/oxide couple dominates in basic melts and that with a progressive basicity reduction the peroxide/superoxide concentration ratio decreases up to only superoxide may exists at sufficiently high values of melt acidity. Therefore, the peroxide ion solubility parameter can be taken for an appropriate measure of Lux-Flood basicity of moderate-to-strong basic carbonate melts by using either eq. (2) or (4).

It is important to outline that a pure O\textsubscript{2} gas cannot be used as titrating gas in carbonate melts as its solubility may be subjected to errors caused by large variations in residual CO\textsubscript{2}, which is invariably present as consequence of the thermal decomposition equilibrium of the carbonate melts (inverse of eq. (1)). Therefore, accurate basicity determinations should require the use of a combined O\textsubscript{2} + CO\textsubscript{2} gas mixture instead of a pure O\textsubscript{2} gas. On the other hand, the addition of the CO\textsubscript{2} gas in the titrating mixture will produce a highly acidic melt in alkali carbonates or their mixtures as CO\textsubscript{2} is the strongest acid in these melts [15] with all the oxide ions being consumed by CO\textsubscript{2} and not by O\textsubscript{2}. Very differently, the fact that large amounts of peroxide ion are still detectable under relatively high CO\textsubscript{2} partial pressures (PCO\textsubscript{2} > 0.2 atm [2]) after addition of rare earth oxides to the alkali carbonates undoubtedly indicates that the acidity strength of CO\textsubscript{2} is decreasing in these mixed carbonates at a level where the two conjugate acid-base pairs of eq. (4) form a strong oxide buffered melt. In these conditions, a part of the oxide ions will react with the O\textsubscript{2} gas to produce peroxide ions in the melt allowing the oxygen solubility data taken under predetermined O\textsubscript{2}-CO\textsubscript{2} mixtures [2] to be used also for an accurate basicity titration up to the peroxide end-point equilibrium.

EXPERIMENTALS

In order to use the peroxide parameter as a quantitative probe for carbonate basicity it is necessary to distinguish the peroxide contribution from the total oxygen solubility data. As this is the type of problem that can be well addressed with the O\textsubscript{2} solubility titration method already described in detail in preceding papers [1,2], the description of the method is dispensed here. However, for the specific purposes of this work, it may be worth remarking how the peroxide concentration has been estimated from the experimental data. As already said, the O\textsubscript{2} solubility method is based on the direct determination of the amount of Cr\textsuperscript{6+} ion, which is then conveniently expressed in terms of its molecular oxygen equivalent calculated according to the following balanced equation [1]:

\[
\frac{3}{4}O_2 + Cr^{3+} + \frac{5}{2}CO_3^2 = CrO_4^{2-} + \frac{5}{2}CO_2
\]  

(7)

Therefore, the peroxide concentration is simply the double of the oxygen solubility value, as evident from the reaction stoichiometry of eq. (2).

Carbonate melt compositions used in the present work for the basicity calculations have been taken from those shown in Table I. The values of equilibrium constants of the various oxygen dissolution mechanisms are also collected in the Table I, which includes the values for K\textsubscript{d} constants that are at the basis of the present basicity calculations.

CALCULATION PROCEDURES AND RESULTS

As already said, the inverse of eq. (1) defines the thermal decomposition reaction of the carbonate salt. The self-dissociation constant (K\textsubscript{d}) varies with the nature of the metallic counter-cation, which therefore determines the amount of oxide ion activity in the melt (i.e., the degree of Lux-Flood basicity).

According to the definition, thermodynamic (or true) K\textsubscript{d} is simply:

\[
K_d = \frac{a_{O_2} p_{CO_2}}{a_{CO_2}^2}
\]  

(8)

where \(a_{O_2}\) and \(a_{CO_2}\) denote the activity of the oxide and of the carbonate ion species in the melt, respectively. For a single carbonate salt, the approximation \(a_{CO_2} = 1\) is reasonable.

Besides, assuming only small concentrations of oxide ions produced by the self-ionization process, the oxide ion activity may be approximated by mole fractions. This results in the definition of an apparent self-dissociation constant (in the following denoted as K\textsubscript{d}\textsuperscript{*}) as:

\[
K_{d*} = [O_2]^2 p_{CO_2}
\]  

(9)

In analogy with the chemistry of aqueous solutions, the Lux-Flood basicity for a carbonate salt may be defined as:

\[
pO_2^2 = -lg [O_2^2] = \frac{\Delta G^o}{2.303RT} + lg p(CO_2) = pK_{d*} + lg p(CO_2)
\]  

(10)

Thus, the basicity scale extends from \(pO_2^2 = pK_{d*}\) (or \(lg p(CO_2) = 0\) for the most acidic medium to \(pO_2^2 = -pK_{d*}\) (or \(lg p(CO_2) = -pK_{d*}\)) for the most basic medium. The Andersen’s doctoral thesis is the most systematic source of available data for carbonate self-dissociation constants [15]. This author reported \(pK_{d*}\) values for single Li\textsubscript{2}CO\textsubscript{3}, Na\textsubscript{2}CO\textsubscript{3} and K\textsubscript{2}CO\textsubscript{3} salts at 923K as 4.69, 9.41 and 11.90, respectively indicating that Li\textsubscript{2}CO\textsubscript{3} is a stronger base than Na\textsubscript{2}CO\textsubscript{3} and much stronger than K\textsubscript{2}CO\textsubscript{3}.

Binary eutectic alkali mixtures are generally used as electrolytes in high temperature fuel cells because of their conveniently low melting points. Typical electrolytic compositions are (62+38) mol % (Li+K)CO\textsubscript{3} and (53+47) mol % (Li+Na)CO\textsubscript{3}. As they do not form ideal mixtures, the self-dissociation constants reported by Andersen on the basis of linear additive functions of the single carbonate thermodynamic properties are to be intended as apparent constants [15]. With the assumption of ideal behavior, basicity may be conveniently defined for a generic A+B salt mixture, as:

\[
pO_2^2 = -lg \left( \left[ O_2^2 \right]_A + \left[ O_2^2 \right]_B \right) = pK_{d*,AB} + lg p(CO_2)
\]  

(11)
According to the Andersen data [15], the acidity level of such eutectics is as respectively $K_d+$ 8.19 and 6.94 for the (Li+K) and (Li+Na) carbonates, which is in the between that of the pristine salts.

Interestingly, in some recent studies the “true” self-dissociation constants (i.e., $K_d$) have been determined with methods that take into account the non-ideality of alkali carbonate eutectics. In the method proposed by the Cassir group, the thermodynamic properties of a solid Li$_2$O in equilibrium with molten Li$_2$CO$_3$ were used to obtain the self-dissociation constants of binary carbonate systems [16-19]. In fact, in (Li+K) and (Li+Na) carbonates the basicity is defined by the Li$_2$O properties as this is the first to precipitate in basic media due to its lowest solubility among all the alkali oxides. Activity values for the Li$_2$CO$_3$ salt in the (Li+Na) or (Li+K) eutectics, also necessary for $K_d$ calculations, were deduced on the basis of a regular solution model with data published in Ref. [20].

As previously mentioned, the determination of the peroxide anion as a major reactive oxygen species dissolved in the La$_2$O$_3$ -containing alkali carbonates provides a strong evidence that in general rare earth additives promote a basic carbonate medium even under relatively high CO$_2$ partial pressure conditions. In absence of activity data available for Li$_2$CO$_3$ in such mixed lanthanum-alkali carbonate systems and also for a direct comparison with the large body of data published in [15], an ideal behaviour will be assumed here and therefore the calculated dissociation constants are always to be intended as apparent constants $K_d+$.

From this assumption, it derives that not only the self-dissociation process, but also any chemical equilibrium between the various oxygen species will be described in terms of apparent constants, unless specified otherwise.

With these premises, the eq. (2) can be used to explicitate the dependence of oxide ion concentration from the peroxide as follows:

$$[O^{2-}] = \frac{[O_2^{2-}]}{K_2 p_{O_2}^{0.5}} \quad (12)$$

Reliable values that are available for $K_2$ have been determined only by Andersen in the ternary (Li+Na+K) system over the temperature range 800-1050K [15] and are expressed in atm$^{-0.5}$ as follows:

$$\log K_2 = \frac{1800}{T} - 2.98 \quad (13)$$

In absence of any other experimental data, the $K_2$ constant value derived from eq. (13) was assumed to be valid for any alkali carbonate systems.

From the definition of melt basicity as:

$$K_d+ = [O^{2-}]_p p_{CO_2} \quad (14)$$

$K_d+$ can be rewritten as combination of eqs. (12)-(14) as follows:

$$K_d+ = \frac{p_{CO_2}[O_2^{2-}]}{p_{O_2}^{0.5} K_2} \quad (15)$$

The eq. (15) states that $K_d+$ of a basic carbonate can be determined through analytical determinations of the equilibrium peroxide concentration at a given $pO_2$ and $pCO_2$ mixture by assuming valid the Andersen data for the constant $K_2$.

It is also possible to calculate $K_d+$ directly from the $K_4$ peroxide solubility constants by using eq. (4), namely by explicitating the partecipation of the CO$_2$/CO$_3^-$ acid-base conjugate pair.

After turning the $K_4$ values reported in Table 1 (as mol ppm x cm$^{1.5}$ x atm$^{0.5}$) into $K_4$ (as mole fractions x atm$^{0.5}$), the following simple relation is obtained to determine $K_d+$:

$$K_d+ = \frac{K_4'}{K_2} \quad (16)$$

The use of either eq. (15) or (16) to measure Lux-Flood basicity has been preliminarily verified with the single Li$_2$CO$_3$ carbonate, a salt of known basicity and for which the gaseous oxygen dissolves exclusively as peroxide [1, 15, 21]. Thus, for instance, using the experimental data reported in [1], we deduce at 1073 K (800°C) a molecular oxygen equivalent value of 0.27 mol ppm cm$^{-3}$ (at PCO$_2$=0.2 atm; PO$_2$=0.8 atm) corresponding to a peroxide concentration of 0.54 mol ppm cm$^{-3}$. The $K_4$ value is 0.12 mol ppm cm$^{-3}$ atm$^{-0.5}$ [1], which becomes $K_4 = 4.8x10^6$ (in mole fraction x atm$^{0.5}$) by using the relation between $K_4$ and $K_4'$, as indicated in Table 2. Introduction of $K_4$ in the eq. (16) or alternatively of peroxide concentration into eq (15) yields a $K_d+$ = 4.00, which is fully consistent with the Andersen data [15]. The Fig. (2) shows the Andersen original plot where it is clearly

### Table 2. Basicity Properties of Lithium-Sodium and Lithium-Potassium Eutectic Carbonates Mixed with 0.5 mol % of La$_2$O$_3$, at 923 K. For Reference, Basicity Calculation for the Single Li$_2$CO$_3$ Salt at 1073 K is also Reported. Basicity is Expressed in Terms of $K_d+$, which is the Apparent Equilibrium Constant for the Carbonate Self-Dissociation Reaction (1)

<table>
<thead>
<tr>
<th>Melt Composition (mol %)</th>
<th>$K_d+$ (mol ppm x cm$^{1.5}$ x atm$^{0.5}$)</th>
<th>$K_d+$ (mol fraction x atm$^{0.5}$)</th>
<th>$K_d+$ (atm$^{0.5}$)</th>
<th>$K_d+$ (mol fraction x atm)</th>
<th>$K_d+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(53Li+47Na+0.5La$_2$O$_3$)</td>
<td>1.08</td>
<td>4.4x10$^{-5}$</td>
<td>0.11</td>
<td>4.1 x10$^{-4}$</td>
<td>3.40</td>
</tr>
<tr>
<td>(62Li+38K+0.5La$_2$O$_3$)</td>
<td>0.16</td>
<td>8.0x10$^{-6}$</td>
<td>0.11</td>
<td>7.2 x10$^{-5}$</td>
<td>4.15</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>0.12</td>
<td>4.8x10$^{-6}$</td>
<td>0.05</td>
<td>9.6 x10$^{-5}$</td>
<td>4.00</td>
</tr>
</tbody>
</table>

$^a$Experimental data taken from Refs. [1, 2].

$^b$Equilibrium constant $K_d+$(mole fraction x atm$^{-0.5}$) is related to $K_d+$ by: $K_d+ = K_d M/\rho$, where $\rho$ is density of the salt (g/cm$^3$) and $M$ is the molecular weight of the salt. Appropriate data have been taken from Ref. [33].

$^c$Experimental data referring to the ternary eutectic LiNaK system (43.5Li+31.5Na+25.0K), after Ref. [15]. To be noted that the $K_2$ constant reported for the Li$_2$CO$_3$ salt is calculated at 1073K.
seen an excellent agreement between our determination at 1073 K and the Andersen data computed from JANAF thermodynamic table, although the most widely cited Andersen data are those computed on the basis of a chemical analysis technique which indicate a more basic salt ($K_d = 3.30$, at 1073 K).

After this initial check, $K_d$ values have been calculated for La$_2$O$_3$-containing (Li+Na) and (Li+K) carbonates by starting from the $K_d$ equilibrium constants reported in Table 1. The results of our calculations are summarized in Table 2. The $K_d$ values for both the carbonate systems confirm that addition of La$_2$O$_3$ promotes the formation of a basic medium, which is more relevant in the eutectic (Li+Na) carbonate.

**DISCUSSION**

Using the basicity definition for a salt mixture given by eq. (11) it is not surprising that a small addition of a basic oxide such as La$_2$O$_3$ to the relatively acid binary eutectic carbonates may have resulted in a dramatic change of basicity. In fully rigorous terms, the eq. (11) implicitly assumes that La$_2$O$_3$ completely dissociates into La$^{3+}$ and O$_2^-$ ions in the molten carbonates and do not form intermediate species. However, thermal analysis studies indicate that La$_2$O$_3$Co$_2$ is the predominant lanthanum carbonate in the temperature range 973-773K [3]. This indicates that La$_2$O$_3$ is a strong base only for the loss of the first oxide ion, whereas is a weak base for the second and the third ionization. Therefore, to better understanding the effect of La$_2$O$_3$ addition on the melt basicity, a general scheme that describes the possible dissolution La$_2$O$_3$ products is proposed.

In general, La$_2$O$_3$ solubility in molten carbonates is very high being ca. $1.0 \times 10^{-2}$ mole fraction at 923K in (Li+Na) carbonate [3,4]. Likewise most important oxides, also the La$_2$O$_3$ decomposition process in molten carbonates has been demonstrated to be a function of melt basicity, which implies the formation of acidic and basic solutes of this oxide upon its dissolution [3].

In presence of a CO$_2$-rich environment, La$_2$O$_3$ is thought to convert to lanthanum carbonate, La$_2$(CO$_3$)$_3$, through a stepwise carbonation process via intermediate formation of soluble lanthanyl carbonates, La$_2$O$_2$CO$_3$ and La$_2$O(CO$_3$)$_2$ [22,23], according to the following likely scheme:

\[ La_2O_3 + CO_2(g) \rightleftharpoons La_2O_2CO_3 \]  \[ La_2O_2CO_3 + CO_2 = La_2O(CO_3)_2 \]  \[ La_2O(CO_3)_2 + CO_2 = La_2(CO_3)_3 \]

The eqs. (17)-(19) represent three conjugate acid-base pairs with eq. (17) being the most complete dissociation equilibrium in the proposed dissolution La$_2$O$_3$ scheme. The increasing melt basicity of alkali carbonate melts by addition of La$_2$O$_3$ can be thus related to the buffering properties of the La$_2$O$_2$CO$_3$ carbonate. The La$_2$O$_2$CO$_3$ thermodynamic dissociation constant (i.e., $K_d$) can be estimated from available thermochemistry data by using the relationship:

\[-2.3RT \log K_d = \Delta H_d - T \Delta S_d \]

Within the temperature range 773-1190 K, the median enthalpy and entropy of the oxy-carbonate decomposition in air atmosphere has been reported to be 145.5 ± 5.0 kJ mol$^{-1}$ and 119.2 ± 5.0 J mol$^{-1}$K$^{-1}$, respectively [23]. At 923K, these values yield a $K_d$ of 2.02, which also indicates the highly basic nature of La$_2$O$_2$CO$_3$.

In accordance with recent published data [24,25], rare earth elements may form stable peroxy-carbonate compounds in peroxide-containing aqueous environments. Hence, the existence of a peroxy-carbonate species La$_2$O$_2$(CO$_3$)$_2$ also in a basic molten carbonate, where peroxy ions are abundant, is worth to be examined.

There is very little information in literature that examines the chemistry of the lanthanyl oxo-cation (i.e., $La_2O_3^{2+}$) or more in general of the 4f electron elements with oxygen donor ligands in molten systems [26,27]. The majority of published work on the oxophilicity properties of f-electron metals has concentrated on the 5f actinide family with the chemistry of the uranyl oxo-cation ($UO_2^{2+}$) being the most studied for its importance in the spent nuclear fuel reprocessing industry. As strong similarities between the lanthanyl and uranyl oxo-cations might be expected from size and charge considerations, the known uranyl coordination chemistry may be used to modelling the behavior of the lanthanyl cation. Formation of stable tricarbonate uranyl complexes \[ \left[ \left( UO_2^{2+}\right) \left( CO_2^{2-}\right) \right]^{3+} \] is well established from the aqueous chemistry of uranium [28,29]. The addition of peroxy to an alkaline carbonate solution promotes the formation of mixed peroxy-dicarbonate uranyl complexes \[ \left[ \left( UO_2^{2+}\right) \left( O_2^{2-}\right) \left( CO_3^{2-}\right) \right]^{3+} \] indicating that peroxy is also a facile ligand capable of displacing one carbonate group [30]. Recently, it has been demonstrated that a similar anionic

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**Fig. (2).** Plot showing the apparent dissociation constant values in molten Li$_2$CO$_3$ plotted versus the reciprocal Kelvin temperature: the single value at 1073 K determined in this study with the gas solubility method is compared with the two data sets derived from Ref. [15]. (The chemical analytical technique described in Ref. [15] consists in the determination of the oxide content in the melt by a pH-metric titration of an aqueous solution containing a pulvurized carbonate melt sample).
peroxo-carbonate complex can also form in alkali carbonate melts under basic conditions as reported in [31]. As peroxo-carbonate can be seen as an adduct product formed by addition of peroxide ion with carbon dioxide, these results seem to indicate that the hypothesis of a peroxo-carbonate existence stabilized by presence of lanthanyl group may be plausible. The following acid-base equilibrium can be considered:

\[ \text{La}_2\text{O}_3\text{CO}_3 + \text{CO}_2 + 0.5\text{O}_2 = \text{La}_2\text{O}_2(\text{CO}_3)_2 \] (21)

In this reaction \text{La}_2\text{O}_3\text{CO}_3 is an amphoteric oxide with a slightly prevalent net basic effect. As the thermal stability of rare earth peroxy-carbonates is reported to decrease rapidly above 873 K (600°C) [24], the involvement of this reaction in the \text{La}_2\text{O}_3 dissolution process is expected to be more relevant at decreasing melt temperatures.

As the extent of the Lux-Flood basicity change upon \text{La}_2\text{O}_3 dissolution was found to be comparatively less in (Li+K) carbonate, this would signify that melt composition may alter to some extent the relative concentrations of lanthanum species in solution probably through electrical field effects. As the field strenghet may be related to the average cation size of the carbonate mixture [31], the latter parameter has been determined as a weighed sum from the known ion radius of each cation multiplied for its mole fraction in the carbonate mixture. The average cation size of the two alkali carbonate mixtures used in this work are 0.88 Å for the (Li+Na) and 0.92 Å for the (Li+K) carbonate. The higher electrical field strenght of the (Li+K) carbonate could therefore reduce the stability of \text{La}_2\text{O}_3\text{CO}_3 in this melt and favour its decomposition towards a most thermodynamically stable form of lanthanum carbonate, namely \text{La}_2\text{O}_2(\text{CO}_3)_3.

By contrast, \text{La}_2\text{O}_3 may dissolve also with a basic mechanism in a \text{CO}_2-	ext{lean} environment. The following simple basic dissolution path has been suggested [3]:

\[ \text{La}_2\text{O}_3 + 3\text{CO}_2^{-} = 2\text{LaO}_3^{2-} + 3\text{CO}_2 \] (22)

However, this reaction model is strongly open to question as eq. (22) predicts a theoretical \text{CO}_2 dependence of -1.5 for the \text{La} solubility, whereas the much lower observed \text{CO}_2 dependence (about a slope of -0.6 in a log-log plot [3]) suggests a more complex mechanism likely involving the peroxide radicals, which are abundant in a basic carbonate. More specifically, the following basic dissolution mechanism is thought to be more plausible:

\[ \text{La}_2\text{O}_3 + 2\text{O}_2^{2-} + \text{CO}_3^{2-} = 2\text{LaO}_3^{2-} + 2.5\text{O}_2 + \text{CO}_2 \] (23)

This reaction should proceed with evolution of both \text{O}_2 and \text{CO}_2 gases and the theoretical \text{CO}_2 dependence of -0.5 is in good precision with the reported -0.6 value [3].

On the other hand, there could be a possibility that a different basic dissolution path would be also operating in a decreasing basic carbonate where larger amounts of peroxide ions are present:

\[ \text{La}_2\text{O}_3 + 2\text{O}_2^{2-} + 2\text{CO}_3^{2-} = 2\text{LaO}_3^{2-} + 1.5\text{O}_2 + 2\text{CO}_2 \] (24)

In this case, the theoretical \text{CO}_2 dependence of the \text{La} solubility is predicted to be higher (i.e., -1.0) than in the previous case. A study of the \text{La} solubility as a function of \text{CO}_2 (and also of \text{O}_2) should allow to precise whether peroxide ions are effectively involved in the basic dissolution of \text{La}_2\text{O}_3.

In summary, the above data have shown that the Lux-Flood acid-base properties of alkali carbonate melts may be significantly modified by slight modification of the melt composition using additives such as \text{La}_2\text{O}_3 or, more in general, rare earth oxides. From a practical perspective, the results of this work may assist in designing high performance electrolytes for Molten Carbonate Fuel Cell technology. In fact, the oxide buffering power of these carbonate mixtures is expected to strongly inhibit hot corrosion processes involving acidic or basic oxide fluxing phenomena of the currently-used engineering materials. However, it is evident that much more information is needed on relevant physico-chemical properties of these carbonate mixtures for such electrolyte applications. Finally, the rare earth incorporation in alkali molten carbonate formulations may have other important implications for such molten salts when used as reaction media or catalyst. For instance, it is speculated that the formation of a very basic media, where peroxide ion can be easily stabilized, could have interesting catalytic properties for the oxidative coupling of methane [32].

**CONCLUSIONS**

In this work a gas solubility method has been applied to measure the Lux-Flood basicity of alkali molten carbonates mixed with \text{La}_2\text{O}_3 by using the oxygen gas as an acidic titrating agent for oxide concentration determinations. As peroxide species are the most stable form of oxygen species in basic carbonate media, only the portion of oxygen gas dissolved in the melt as peroxide has been used as a qualitative probe for the basicity determinations.

From analysis of the experimental results, it could be deduced that the Lux-Flood basicity level of alkali carbonate mixtures are being dramatically modified by small additions of \text{La}_2\text{O}_3 to the melt with the greatest basicity changes observed when \text{La}_2\text{O}_3 is added to a binary lithium-sodium eutectic carbonate.

The high Lux-Flood basicity values of the mixed \text{La}_2\text{O}_3-alkali carbonate melts is in accordance with the known strong basic character of rare earth oxides. Plausible routes for the dissolution of \text{La}_2\text{O}_3 in molten carbonates under both acidic and basic regimes have been proposed for a better understanding of the \text{La}_2\text{O}_3 effects on molten carbonate basicity. Acidic dissolution of \text{La}_2\text{O}_3 is suggested to take place through a stepwise carbonation process leading to \text{La}_2(\text{CO}_3)_3 via intermediate formation of strongly basic lanthanyl carbonates species like \text{La}_2\text{O}_2\text{CO}_3 and \text{La}_2\text{O}(\text{CO}_3)_2. The basicity changes are dependent on the relative proportions of the individual lanthanum species in solution, which, in turn, depend on the melt composition with an observed reduction of the overall melt basicity at increasing average cation radius of the alkali carbonate mixture (from lithium-sodium to lithium-potassium carbonate).

In view of strong affinities with the chemistry of the uranyl ion, \text{La}_2\text{O}_3 dissolution is presumed to proceed also with formation of stable lanthanyl peroxo-carbonate complexes as similar uranyl complexes have been already described in literature. As rare earth peroxo-carbonates decompose in air
above 873 K, this dissolution path is expected to be more relevant at decreasing melt temperatures.

In absence of CO₂, basic dissolution of La₂O₃ takes place leading to the formation of soluble lanthanate species (i.e., LaO₂⁺). It is suspected that peroxide ions are involved in the basic dissolution mechanism of La₂O₃.

REFERENCES