COMPARATIVE BEHAVIOUR OF OXYGEN ELECTROCHEMICAL SYSTEMS IN MOLTEN ALKALI CARBONATES AT 500-750°C

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ABSTRACT

The behaviour of reduced oxygen species in Na-K, Li-K, Li-Na and Li-Na-K molten carbonate eutectics, is investigated thermodynamically and by the means of electrochemical methods. Thermodynamic predictions are in good agreement with experimental results. It is shown that, in all the studied melts, peroxide ions are stabilized in basic media (O_2^{2-}/O_2^- system is characterized). Superoxide species is never stabilized in lithium-containing carbonate melts whatever the selected conditions. This species is stabilized in Na-K melt, in slightly basic media. O_2/O_2^{2-} system is evidenced and characterized. CO_2 species never participates in the rate-determining reduction steps.

STATE-OF-THE-ART

Chemical properties of molten alkali carbonates, generally used in fuel cells, are influenced by the existence of reduced oxygen species and their electrochemical behaviour. Catalytic effects of these media in the oxidative transformation of methane into ethane and ethylene are correlated with the stability of peroxide and superoxide species (1-5).

An abundant literature has been dedicated to oxygen reduction in molten alkali media (6-17). It is well admitted now that, according to the considered molten carbonate, O_2^{2-} and/or O_2^- species are involved in the reduction process. Several and controversial hypotheses have been formulated on the reduction mechanisms and in particular, whether or not CO_2 species participates in the rate-determining step of this process. In Li-K molten carbonate, the most investigated alkali carbonate melt, Appleby et al (6) postulated, on the basis of reaction orders, the reduction of peroxide species with carbon dioxide, followed by the direct reduction of superoxide. In the same melt, Vogel et al observed a single wave that they ascribed to a 3-electron reduction of superoxide species (11). In Na-K carbonate melt, Appleby et al (6) attributed the two reduction currents observed to: O_2^{2-} + 2 CO_2 + 2e^- ⇔ 2 CO_3^{2-} and O_2^- + e^- ⇔ O_2^{2-} respectively. In the same eutectic, Uchida et al (9) proposed a first superoxide...
path: $O_2^- + 2 CO_2 + 3e^- \leftrightarrow 2 CO_3^{2-}$ followed by the direct reduction of superoxide species: $O_2^- + e^- \leftrightarrow O_2^{2-}$. Other interpretations have been given by us for the two mentioned eutectics (14,15). In the case of Na-Li-K (12,16) and Li-Na (13,17) molten carbonate eutectics, it has been shown that, in basic media, peroxide is the only stable reduced oxygen species and that the reduction reaction is: $O_2^{2-} + 2e^- \leftrightarrow 2 O_2^{2-}$.

In this paper, a synthetic study, partially based on previous works (14-17), was developed to elucidate the redox mechanisms of oxygen reduction in different molten carbonates and compare the behaviour of these melts, according to the nature of alkaline ion. A thermodynamic study allowed to describe the stability of reduced oxygen species at different temperatures and acidity levels. Electrochemical techniques were used to investigate oxygen redox systems and determine different experimental parameters (solubilities, diffusion coefficients, reaction rates etc.).

THERMODYNAMIC APPROACH

Thermodynamic data concerning the molten carbonate melts presented in Table I are deduced from thermochemical tables (18,19) and from Andersen's experimental data (20).

Table 1- Composition and melting points of the alkali molten carbonates investigated.

| Eutectic                 | composition mol.% | melting point °C |
|--------------------------|-------------------|-----------------|
| Li$_2$CO$_3$.Na$_2$CO$_3$ | 53.3-46.7         | 496             |
| Li$_2$CO$_3$.K$_2$CO$_3$  | 50-50             | 504             |
| Na$_2$CO$_3$.K$_2$CO$_3$  | 36-44             | 710             |
| Li$_2$CO$_3$.Na$_2$CO$_3$.K$_2$CO$_3$ | 43.5-31.5-25 | 397             |

Characteristic dissociation equilibria and thermodynamic self-ionization constants have been described elsewhere (14-17). Na-K carbonate eutectic is an ideal mixture (21). In the case of Li-K, Li-Na and Li-Na-K melts, which do not form ideal liquid solutions, the activity coefficients were determined on the basis on Lumsden data (21). The accessible acidity domain, defining the limits between the most acidic medium (P(CO$_2$) set at one atm.) and the most basic medium (molten salt saturated with oxide species) is defined by the constant pK$_{d^*}$:

$$pK_{d^*} = - \log a(M_2O) - \log P(CO_2)$$

(152)

(152) unless CC License in place (see abstract).
Table 2- Evolution of the accessible acidity range (pKd*) with temperature for the molten carbonate eutectics investigated in this study (18).

| T(°C) | Na-K | Li-K | Li-Na | Li-Na-K |
|-------|------|------|-------|---------|
| 450   |      |      |       | 7.44    |
| 500   | 6.56 | 6.56 | 6.56  |         |
| 550   | 5.83 | 5.84 | 5.84  |         |
| 600   | 5.18 | 5.22 | 5.23  |         |
| 650   | 4.71 | 4.73 | 4.74  |         |
| 700   | 4.30 | 4.33 | 4.34  |         |
| 750   | 9.09 | 4.18 | 3.89  | 3.91    |
| 850   | 7.80 | 3.43 | 3.16  | 3.18    |
| 927   | 6.98 | 2.93 | 2.68  | 2.70    |

Acidity-potential diagrams have been established as previously described (the oxygen electrode was taken as a reference) (14,16). The oxidation of the molten eutectic is characterized by the following electrochemical systems: \( \text{O}^2-/\text{O}_2^- \) and \( \text{O}_2^-/\text{O}_2^2^- \). Electrochemical stability diagrams have been contracted for the different eutectics. Figure 1 shows, for instance, the diagram of Li-Na-K melt at 550°C, with the oxidation reactions (\( \text{O}_2 \) or \( \text{O}_2^2^- \) formation), the reduction reactions with (K, CO or C formation), the acidity limit (CO\(_2\) set at one atm.) and the basicity limit (Li\(_2\)O precipitation). Under the experimental conditions given (even at very low oxygen pressures, \( P(\text{O}_2) = 10^{-3} \) atm.), \( \text{O}_2^2^- \), stabilized in basic media, is the only reduced oxygen species present in this molten eutectic. \( \text{O}_2^- \) species is never present in significant amounts. The same behaviour has been observed for Li-Na and Li-K carbonate eutectics containing lithium ions. In the case of the Na-K melt, peroxide species is stabilized in basic media, whereas superoxide species can be stabilized in moderately basic or moderately acidic media. These interpretations are in agreement with the results obtained by Andersen in his experimental thermodynamic study of molten alkali carbonates.

**ELECTROCHEMICAL STUDY**

All the molten carbonate eutectics mentioned in Table I and sodium oxide were Merck reagents of analytical grade (>98% purity). Sodium peroxide was a Prolabo reagent (94% purity) and lithium oxide was a Johnson Matthey reagent (95% purity). The working electrodes were gold planar and gold wires. The auxiliary electrode was a gold wire. The reference electrode was a silver wire dipped into an Ag\(_2\)SO\(_4\) (10\(^{-1}\) mol./Kg) eutectic melt. The electrochemical apparatus, cell and conditions used in this investigation were described in previous works (15).

Reduced oxygen systems were characterized by the means of different electrochemical techniques at a gold electrode: hydrodynamic and cyclic voltammetry, chronoamperometry, chronopotentiometry and convolution potential sweep methods. In all the molten carbonates studied, the formation of peroxide or superoxide species is due to the reaction of molecular oxygen with oxide or carbonate ions (6). The instability of
molecular oxygen in such media was pointed out in most of the electrochemical publications (6-17), as well as in experimental thermodynamic studies (20).

The behaviour of molten carbonates is greatly dependent on the acidity of the medium. No reduction currents representative of reduced oxygen species were observed in acidic media. Reduction currents of these species appeared in slightly basic or basic media, according to the nature of the molten eutectic.

In the case of the Na-K eutectic, a two-electron reduction current attributed to peroxide species was observed:

\[ \text{O}_2^{2-} + 2e^- \leftrightarrow 2 \text{O}_2^- \]

This system was analyzed in a previous study (14). When the acidity of the melt increased, the reduction current of peroxide species progressively disappeared and another reduction current corresponding to superoxide species was observed at a higher potential:

\[ \text{O}_2^- + e^- \leftrightarrow \text{O}_2^{2-} \]

Fig. 2 shows these reduction currents at two acidity levels.

In Li-K, Li-Na and Li-Na-K eutectics, experimental evidence was given for the existence of \( \text{O}_2^{2-} \) species in basic media, as predicted thermodynamically. \( \text{O}_2^- \) species was never observed whatever the selected conditions. Cyclic voltammetry and convolution potential sweep techniques were performed to describe the \( \text{O}_2^{2-}/\text{O}_2^2^- \) system. Theoretical equations describing the convolutive transformation of cyclic voltammograms were developed for non-unity systems (16).

The voltammogram obtained after addition of sodium peroxide in Li-K melt at 650°C is given in Fig. 3. Cathodic and anodic peaks are attributed to \( \text{O}_2^{2-}/\text{O}_2^- \) system.

In the case of Li-Na carbonate eutectic, peroxide reduction was evidenced by cyclic voltammetry (Fig. 4) and convolution potential sweep voltammetry at 750°C, confirming the results of Tomczyk et al (13). No oxidation current relative to oxide ions was detected, probably because it occurred at a potential very close to the anodic limit of the medium. Fig. 5 shows a stationary voltammogram at 750°C, obtained by transformation of the cyclic voltammogram of Fig. 4. This result is in agreement with that of White et al (12). Fig. 6 shows the evolution of the reduction current with the amount of peroxide ions, allowing the determination of the solubility of \( \text{Na}_2\text{O}_2 \).
In all the molten eutectics, it was shown that there was no potential shifts corresponding to the reduction of peroxide or superoxide species with the acidity of the medium (important shifts are predicted thermodynamically when CO$_2$ species is included in the reduction paths) (14-17). This observation was confirmed, in the case of Li-Na and Na-K melts, by the determination of very low rate constants of neutralization reactions of CO$_2$ by oxide or peroxide species. Therefore, it can be concluded that CO$_2$ did not participate in the rate-determining reduction steps.

Table III summarizes all the results obtained with the four molten carbonate eutectics.

| Parameters       | Na-K 750°C | Li-K 650°C | Li-Na 750°C | Li-Na-K 500°C |
|------------------|------------|------------|-------------|---------------|
| $O_2^2-$ stability | basic media | basic media | basic media | basic media   |
| $O_2^-$ stability | intermediate acidity | unstable | unstable | unstable |
| $O_2^2-/O_2^-$   | rapid $E_0 = -0.25$ V/(Ag$^+/Ag$) | rapid $E_0 = -0.70$ V/(Ag$^+/Ag$) | rapid $E_{1/2} = -0.38$ V/(Ag$^+/Ag$) (only $O_2^2- + 2e^- \rightarrow 2O_2^-$) | rapid $E_{1/2} = -0.23$ V/(Ag$^+/Ag$) |
| $O_2^-/O_2^2-$   | $E_{1/2} = -0.21$ V/(Ag$^+/Ag$) (only $O_2^- + 1e^- \rightarrow O_2^{2-}$) | | | |
| $S(\text{Na}_2\text{O})$ or $S(\text{Li}_2\text{O})$ | 3.0 $10^{-2}$ mol/Kg | 8.0 $10^{-2}$ mol/Kg | | |
| $S(\text{Na}_2\text{O}_2)$ | 6.7 $10^{-2}$ mol/Kg | 6.8 $10^{-2}$ mol/Kg | | |
| $D(O_2^{2-})$ | 1.5 $10^{-5}$ cm$^2$/s | 1.1 $10^{-5}$ cm$^2$/s | 1.2 $10^{-5}$ cm$^2$/s | |
| $D(O_2^-)$ | 6.8 $10^{-5}$ cm$^2$/s | 1.2 $10^{-5}$ cm$^2$/s | | |
| $\delta(O_2^{2-})$ | 1.2 $10^{-2}$ cm | | | |
| Rate constant $O_2^- + CO_2 \rightarrow$ | 1.45 $10^{-3}$ atm$^{-1}$s$^{-1}$ | | 1.4 $10^{-3}$ atm$^{-1}$s$^{-1}$ | |
| Rate constant $O_2^{2-} + CO_2 \rightarrow$ | 4.4 $10^{-3}$ atm$^{-1}$s$^{-1}$ | | 2.4 $10^{-3}$ atm$^{-1}$s$^{-1}$ | |
CONCLUSION

The results obtained with molten alkali carbonates by electrochemical methods are in accordance with thermodynamic predictions and Andersen's experimental data.

Peroxide species can be stabilized in basic media in all the investigated melts. According to thermochemical data it appears that the stabilization of peroxide species is easier in alkali molten carbonates containing lithium ions (the stability of peroxide species decreases in the following order: Li$_2$O$_2$>Na$_2$O$_2$>K$_2$O$_2$).

Superoxide species are not present in significant quantities in molten carbonates containing lithium ions (KO$_2$>NaO$_2$>LiO$_2$). This species can be stabilized in molten Na-K melt, in slightly basic media.

The rate constants of the neutralization reactions of CO$_2$ by oxide or peroxide species are low enough to consider that CO$_2$ does not participate in the rate-determining reduction steps of O$_2^2-/O^2-$ and O$_2^-/O_2^{2-}$ systems.
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Figure 1. Stability range of Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$ eutectic at 550°C from Janaf Thermochemical Tables (18) under the following conditions: (1) $a(i) = 1$; (2) $a(i) = 10^{-1}$; (3) $a(i) = 10^{-2}$; (4) $a(i) = 10^{-3}$. (A) $P(i) = 1$ atm.; (B) $P(i) = 10^{-1}$ atm.; (C) $P(i) = 10^{-2}$ atm.; (D) $P(i) = 10^{-3}$ atm. $a(i)$ and $P(i)$ represent respectively the activity and the partial pressure of species $(i)$. 

Li$_2$CO$_3$ - Na$_2$CO$_3$ - K$_2$CO$_3$

43.5 - 31.5 - 25 mol%
Figure 2. Voltammograms of molten Na$_2$CO$_3$-K$_2$CO$_3$ at a gold electrode at 750°C under P(O$_2$) = 1 atm. for 25 h and [Na$_2$O] = 0.4 mol./Kg. Bubbling P(CO$_2$) = 0.1 atm. + P(O$_2$) = 0.5 atm. for (a) t = 0; (b) = 3h.

Figure 3. Voltammogram of molten Li$_2$CO$_3$-K$_2$CO$_3$ at a gold electrode at 650°C, after addition of sodium peroxide (C = 1.35 $10^{-2}$ mol./Kg). Ref. Ag$^+$/Ag; v = 200 mV/s; P(argon) = 1 atm.; A = 0.125 cm$^2$. 

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Figure 4. Voltammogram of Li₂CO₃-Na₂CO₃ at a gold electrode at 750°C. P(O₂) = 1 atm. for 48 h; [Na₂O₂] = 1.77 × 10⁻³ mol./Kg + [Li₂O] = 0.53 mol./Kg; Ref. Ag⁺/Ag; v = 200 mV/s; A = 7.8 × 10⁻² cm².

Figure 5. Convolution transformation of the cyclic voltammogram of Figure 4.
Figure 6. Plot of cathodic peak current vs $[\text{Na}_2\text{O}_2]$ (concentration of $\text{Na}_2\text{O}_2$ added), obtained from voltammograms of $\text{Li}_2\text{CO}_3$-$\text{Na}_2\text{CO}_3$ at a gold electrode at 750°C. Ref. $\text{Ag}^+/\text{Ag}$. Argon pressure 1 atm.; $v = 100$ mV/s.