Chemical and structural stability of ceramic materials in molten alkali carbonates is critically evaluated. The materials showing acceptable stability include nickel oxide, cobalt oxide, high density alumina and alkali aluminates. Among the alkali aluminates, lithium aluminate in various high surface area forms has been extensively employed as a support material in molten carbonate fuel cells. A detailed discussion of the stability of lithium aluminate under various conditions is presented.

Molten alkali carbonates (Li2CO3, Na2CO3 and K2CO3 and their binary and ternary mixtures) offer a wide range of physicochemical and kinetic characteristics desirable for electrolytes and reaction media. Melting points of the alkali carbonates can be varied from 400°C for the ternary eutectic to 900°C for K2CO3. Other properties such as viscosity, electrical conductivity and gas solubility can also be varied by suitably changing the compositions of the mixtures [1]. A list of some of the applications, temperature range of the application, mixtures employed, and pertinent references is presented in Table 1.

**TABLE 1. APPLICATION OF MOLTEN CARBONATES**

| Application                  | Temperature Range, °C | Carbonate Mixture        | References |
|-----------------------------|-----------------------|--------------------------|------------|
| Fuel Cell                   | 600- 700              | Binary and Ternary       | 1,2        |
| Thermal Energy Storage      | 400- 600              | Binary and Ternary       | 3          |
| Coal Gasification           | 800-1000              | Na2CO3                   | 4,5        |
| Desulfurization of Gases    | 400- 500              | Ternary                  | 6          |

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Stability of ceramics is of interest in molten carbonate systems because these materials can be used as constituents of various components in these systems. For example, various types of ceramic electrolyte support materials in the form of fine powder and/or fibers have been employed in molten carbonate fuel cells [1]. The support material holds the electrolyte by capillarity and provides a 'paste-like' separator between the electrodes. Additions of ceramics have also been suggested for providing a sintering resistance to porous metal electrodes in the molten carbonate fuel cell environments [7]. Also, the ceramic materials in the form of coatings or bulk can be used as materials of construction for reaction vessels [8]. Ceramics have also been suggested as volume-change-control additives in thermal energy storage applications employing carbonate salts [3].

The behavior of ceramics in contact with the molten carbonates is strongly influenced by

a. Composition of the melt, including minor impurities, and moisture content
b. Surrounding gas environment, especially CO₂, H₂O, SO₂, Cl₂
c. Physical form of the ceramic material, such as powder, fibrous, porous disks, coatings or bulk solid
d. Operating potential and temperature

The available information should therefore be applied with a careful consideration of these factors. A critical evaluation of the available data on chemical and structural stability of various ceramic materials is presented in this paper. For convenience, the ceramic materials are grouped as

a. Single oxides
b. Mixed oxides, and
c. Other non-oxide ceramics

Since lithium aluminate has been used extensively as an inert material in the molten carbonate systems, a detailed discussion of the stability of this material is also included.
1. **Single Oxides**

1.1 Oxides of Alkaline-Earth Metals (MgO, CaO)

The MgO in the form of sintered porous discs [9, 10] or a fine powder [11, 12] has been employed as a support material in the molten carbonate fuel cells. Janz and Coworkers [13, 14], using a simple thermodynamic analysis, predicted that pure MgO should be 'practically' inert against Li₂CO₃, K₂CO₃, and Na₂CO₃ in the temperature range of 750 to 1000°C. Tseung and Tantram [10], however, observed laminar faults in sintered MgO diaphragms in the presence of carbonates. These faults may have been caused, at least partly, by a dissolution of impurities from the diaphragm, but MgO itself may not be as stable as predicted from the simple thermodynamic calculations. Van Velden [15] showed that MgO has a significant solubility in alkali carbonate melts in the presence of CO₂:

\[
\text{MgO(s) + CO}_2\text{(g) ⇌ Mg}^{++}\text{(melt) + CO}_3\text{(melt)}
\]  

(1)

In the ternary melt at 1 atm CO₂ they experimentally measured a 5 mol% molten MgCO₃ at 550°C and a 1 mol% at 700°C. At higher temperatures and larger Li contents, the stability of MgCO₃(melt) decreases. In addition to Reaction 1, water vapor equilibrium may also affect the solubility of MgO:

\[
\text{MgO(s) + H}_2\text{O(g) ⇌ Mg}^{++}\text{(melt) + 2 OH}^-\text{(melt)}
\]  

(2)

Because of the solubility problems, the use of MgO as a support material was discontinued [1].

The behaviour of CaO is similar to that of MgO, i.e., it also shows a finite solubility in the presence of CO₂. Flood, et al. [16] investigated the solubility of CaO in single alkali carbonate melts at temperatures above 900°C. The solubility at a given temperature increased in the order of Li₂CO₃ < Na₂CO₃ < K₂CO₃. At 1 atm CO₂ and 1000°C, the CaCO₃ solubility was estimated to be 27, 37 and 50 mol% respectively in single Li-, Na- and K- carbonate melts. The solubility at lower CO₂ levels, is however, expected to be proportionately lower.

1.2 Oxides of Nickel, Cobalt and Iron

Nickel, cobalt and iron remain stable in a metallic form under a reducing gas environment, such as that encountered on the anode side of the molten carbonate fuel cells [1]. In the oxidizing environment, or at higher (more positive) potentials, oxides of these metals are formed. These oxides
are very stable in the molten carbonate environment. In fact, NiO having surface areas of 0.1 to 1 m²/g has been used as a stable cathode in the molten carbonate fuel cells [1]. It is interesting to note that when the oxide is formed in the presence of Li₂CO₃, Li atom enters into the structure of NiO (Li₅Ni₁₋₅O) and imparts semiconductor properties [17]. The electronic conductivity of such lithiated-nickel oxides is several orders of magnitude greater than that of pure NiO. The experience with the oxides of cobalt and iron has been limited. An iron oxide cathode has been used by SRI [18] in a direct-carbon molten carbonate fuel cell.

1.3 Silica and Quartz

Silica and quartz in direct contact with molten carbonates react readily to form silicates. In the apparatus where a transparent jacket or window is required in a noncontact application, such as in the carbonate vapor environment, quartz may be used for a short period. Eventually, however, the carbonate vapor tends to react with the surface of quartz and the quartz becomes nontransparent.

1.4 Lead Oxide

Lead oxide is one of the few materials that show nonwetting contact angles with carbonate melts. Davis and Kinniburgh [19] experimented with this material in an attempt to find an analogous material to Teflon used at lower temperatures for aqueous media. The lead oxide showed high contact angles (nonwetting) initially, but after several hours, the contact angles approached zero, indicating some reaction with the carbonates.

1.5 Oxides of Zirconium, Titanium and Chromium

Oxides of these metals form mixed oxides with the carbonates. For example [20]

\[ \text{ZrO}_2 + \text{Li}_2\text{CO}_3 \rightleftharpoons \text{Li}_2\text{ZrO}_3 + \text{CO}_2 \] (3)

The chemical equilibrium depends on the activity of CO₂. Broers and Van Ballegoy [21] suggested small additions of ZrO₂ to the carbonate electrolyte to provide a buffer capacity with regard to CO₂.

Titanium oxide has been investigated by IGT [22] in a powder form, but was found unsuitable as an electrolyte support material.
Chromium oxide (Cr$_2$O$_3$) protective layer is generally formed on 300 and 400-series stainless steels. In the presence of carbonates, however, Grantham and Coworkers [23] observed no presence of Cr$_2$O$_3$ film during their examination using X-ray diffraction, X-ray fluorescence, and emission spectrographic techniques. Instead they found a LiCrO$_2$ (predominantly the hexagonal structure) film on the stainless steels. This indicates that LiCrO$_2$ is a stable material in the presence of carbonates. Even if Na$_2$CO$_3$ and K$_2$CO$_3$ are present in the melt, the film was found to be primarily LiCrO$_2$.

1.6 Aluminum Oxide

Alumina has been used extensively as a corrosion resistant material in the presence of carbonates. High density, high purity fused-cast or slip-cast a-alumina is corrosion resistant at temperatures up to 1200°C. (Grantham and Ferry [23]). Low density or amorphous alumina is not corrosion resistant. Alumina with numerous voids or impurities (particularly silica) is disintegrated by the carbonate melts. Grantham and Ferry [23] noted that the external crystal structures of the cast alumina bricks is more corrosion resistant than the internal structure. Therefore, care must be exercised in using these bricks.

To ensure the minimum reaction of the bulk-form alumina with the carbonates, a 'pretreatment' of the alumina with an appropriate carbonate melt is recommended. This pretreatment results in formation of an alkali aluminate that is lower in density as compared with alumina. Thus, for example,

\[ 1 \text{ cc Al}_2\text{O}_3 \rightarrow 1\frac{1}{2} \text{ to } 2 \text{ cc LiAlO}_2 \]

Thus, even if the alumina surface is somewhat porous, or contains some cracks, these cracks are likely to be filled because of the increase in volume after the pretreatment. Thus a passive film of alkali aluminate formed on the surface of Al$_2$O$_3$ appears to be the factor responsible for the excellent stability of bulk-form Al$_2$O$_3$. Interestingly, even aluminum metal hardware has been used in the molten alkali carbonate environment at temperatures up to 600°C [22], in spite of the fact that aluminum melts at 660°C. Again, the protecting layer of Al$_2$O$_3$, subsequently converted to an alkali aluminate may be credited for this stability.

Alumina in a powder form, however, reacts readily with alkali carbonates to form corresponding alkali aluminates. Among the various forms of alumina, γ-Al$_2$O$_3$ is found to be the most reactive and α-Al$_2$O$_3$ the least [38].

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2. Mixed Oxides

2.1 Titanates and Zirconates

Mixed oxides of TiO$_2$ and ZrO$_2$ with alkali carbonates are likely to be stable in the carbonate environment, however their stability is dependent on gas environment as noted in Section 1.5.

Potassium hexatitanate (K$_2$Ti$_6$O$_{13}$), manufactured in a fibrous form, has been used extensively as a separator material in alkali environment at low temperatures. In the molten carbonates, however, this material reacts with carbonates and forms rounded particles, possibly potassium metatitanate.

Calcium titanate (CaTiO$_3$) is expected to be thermodynamically unstable in a carbonate environment [24].

Lithium zirconate may be stable in the carbonate environment, but its stability has not been fully investigated.

2.2 Silicates

Alkali silicates are also soluble in carbonates, as is the case with silica. Russian investigators [25] studied the possibility of using lithium aluminosilicates as inert support materials for carbonate electrolytes. These materials showed cationic conductivity and lower specific resistance than the oxides discussed earlier. The aluminosilicate/carbonate electrolyte also had good mechanical properties. However, the aluminosilicates reacted with the carbonate, as shown from the lowering of melting point of the carbonate phase. Thus, silicates appear unsuitable as inert material in a carbonate environment.

2.3 Aluminates

Magnesium aluminate (MgAl$_2$O$_4$) spinel and magnesia-rich spinel (Mg$_{1+x}$Al$_2$O$_4$) both are expected to be thermodynamically stable in a carbonate environment [24]. The experiments at General Electric, however, with a high surface area powder (~20 m$^2$/g) showed a degradation of MgAl$_2$O$_4$ to LiAlO$_2$ by the reaction [26] -

$$\text{MgAl}_2\text{O}_4 + \text{Li}_2\text{CO}_3 \rightarrow \text{MgO} + 2 \text{LiAlO}_2 + \text{CO}_2 \uparrow.$$ (4)
Calcium aluminate is also a possible candidate material, however, no data on its stability is available.

Alkali aluminates show a good stability in a carbonate environment, as will be discussed in greater detail in Section 4.

2.4 Perovskites

Perovskites (e.g., LaCrO₃) have been employed as stable materials at 800 to 1000°C in solid oxide fuel cells. These materials show significant electrical conductivity and are also likely to be stable in carbonate environment, especially in H₂S-containing environment, and thus these materials appear promising as sulfur tolerant anode materials [26]. Stability of these materials needs to be examined in more detail.

3. Other Nonoxide Ceramics

Boron nitride, B₃N, has been employed as a separator material for high temperature Li/S batteries, where it is used as a matrix. The material has been investigated as a waterproofing agent [19] in a carbonate system, but its waterproofing capabilities are destroyed above 400°C in contact with the carbonates [27].

Titanium carbide, TiC, is expected to be unstable from thermodynamic considerations because it will form an oxide in the presence of carbonates [24].

Tungsten carbide, WC, often used as an electrode material in various fuel cell systems, may be stable in a carbonate environment and may also be tolerant to H₂S-containing gases [28]. The stability data are, however, not available.

4. Alkali Aluminates

Alkali aluminates, particularly the meta aluminates (LiAlO₂, NaAlO₂, and KAlO₂), show a remarkable chemical stability in alkali carbonate melts. As stated in Section 1, the formation of these aluminates is responsible for passivation of bulk Al₂O₃ in the presence of carbonates. Because of their stability, the aluminates have been commonly used in the molten carbonate fuel cells as high surface area inert support materials for electrolyte matrices. As a support material, the aluminates not only have to be chemically stable, but their structural characteristics, i.e., particle shape and size, should also be stable. For optimum mechanical
properties of the matrix, a needle-like shape of the inert particles is desirable [29, 30]. These aspects are discussed below.

4.1 Chemical Stability of Alkali-Metal Aluminates in Carbonates

Broers and Van Ballegoy [21] presented thermodynamic data for aluminates and determined phase diagrams for stability regions of various alkali aluminates with respect to carbonate composition. From their work, the following important points are summarized.

The formation reaction of alkali aluminates (using $\alpha$-Al$_2$O$_3$),

$$\text{Al}_2\text{O}_3 + M_2\text{CO}_3 \rightarrow 2 \text{MAIO}_2 + \text{CO}_2$$

at 725°C has a $\Delta G$ of -54.5 kJ/mol for LiAlO$_2$ and -14.7 kJ/mol for NaAlO$_2$ and KAlO$_2$. Because of the considerably lower free energy, the formation of LiAlO$_2$ is favored relative to NaAlO$_2$ and/or KAlO$_2$. Therefore, LiAlO$_2$ is stable over a wide range of carbonate compositions. The rate of Reaction 4 increases with increasing Al$_2$O$_3$ surface area. Chemical activity of a given Al$_2$O$_3$ phase also affects $\alpha$-Al$_2$O$_3$ being the least active, $\gamma$-Al$_2$O$_3$ and 'amorphous' Al$_2$O$_3$ have greater activity, in the order stated.

By assuming that the activity of individual carbonates in a mixture of alkali carbonates is equal to their ionic fraction, they derived equilibrium composition curves $\phi(T)$ for a coexistence of the corresponding aluminates (Figure 1). The liquidus curve $f(T)$ intersects the equilibrium curve $\phi(T)$ at an invariant point $T_c$. It can be seen in Figure 1A and 1B that in the Li$_2$CO$_3$ - containing binaries, LiAlO$_2$ is the stable phase for Li$_2$CO$_3$ contents greater than 20 to 25%. A similar conclusion was also reached for the ternary carbonate system. Note that the equilibrium curves were derived without a specific reference to different crystal phases (See Section 4.2) of the meta aluminates, or to other possible aluminates [31, 41]. The equilibrium curves should therefore be verified for specific situations by considering all the likely phases and compositions of the aluminates.

A limited solid solubility among mixed aluminates was found, i.e., in a mixed carbonate melt, one alkali aluminate may contain small amounts of other alkalies in its crystal lattice. For example, in a Li$_2$CO$_3$-K$_2$CO$_3$ binary, a saturated solid solution composition of Li$_{0.94}$K$_{0.06}$AlO$_2$ is likely [21]. Such solid solutions, have also been qualitatively verified by X-ray diffraction measurements.
4.2 Phase and Structural Stability of LiAlO₂

The meta-lithium aluminate (LiAlO₂) exists in three different allotropic forms*:

1. α-LiAlO₂ - The structure of this phase as determined by Marezio and Remeika [32] is a hexagonal and of the space group R3m. It is isostructural with NaHF₂, which can be described as a distorted NaCl structure elongated along a threefold axis. The cations are octahedrally coordinated. The lattice parameters are: a = 2.800 Å and c = 14.216 Å, with an X-ray density of 3.401 g/cm³.

2. β-LiAlO₂ - This phase has a monoclinic structure with lattice parameters: a = 8.147 Å, c = 6.303 Å and β = 93.18°, as determined by Chang and Margrave [33]. Their IR spectra studies indicated that Al ions are in both tetrahedral and octahedral coordination. The space group for this phase was not determined. The density as determined from the X-ray data is 2.59 g/cm³.

3. γ-LiAlO₂ - This phase has a tetragonal structure with lattice parameters: a = 5.169 Å and c = 6.268 Å, space group P4₁2₁2 and density 2.615 g/cm³ [34]. γ-LiAlO₂ is piezoelectric [35].

Marezio and Remeika [32, 35] pointed out that like any other LiM₂O₃ compounds, where M can be B, Al, Ga, In, or Tl (Group III elements), γ-LiAlO₂ (lower cationic coordination) can be converted to α-LiAlO₂ (higher cationic coordination) under high temperature and pressure. On the other hand, α-LiAlO₂ transforms easily to γ-LiAlO₂ by heating at 600°C under normal pressure. They considered γ-LiAlO₂ stable and α-LiAlO₂ metastable at low temperatures and normal pressures.

Chang and Margrave [33] synthesized β-LiAlO₂ from a mixture of Li₂O₂ and Al₂O₃ at 18 kbars pressure and 370°C. They also found that the same mixture produced α-LiAlO₂ at 25 kbars and 530°C. However, they could not form γ-LiAlO₂ by heating either α-LiAlO₂ or β-LiAlO₂ at 710°C, as was observed by Marezio and Remeika [35], and they suggested this process may be slow.

The alpha to gamma phase transformation in LiAlO₂ at

* Caution must be exercised regarding the nomenclature of various LiAlO₂ forms, as different investigators use different designations. In this paper we will follow the nomenclature as described in this text.
elevated temperatures was also observed by other investiga
tors [22, 36, 37]. This process is irreversible at normal
pressure, and the reverse reaction can only be achieved by
applying pressure or by grinding followed by heating [38].
At much higher temperatures (~1300°C), LiAlO₂ transforms [38]
to LiAl₅O₈. Recently Stork and Pott [37] have reported a
decomposition LiAlO₂ to LiAl₅O₈ at temperatures as low as
800°C.

Thus, starting with α-LiAlO₂, transformation to γ-LiAlO₂
occurs at about 600°C, and further heating above 1300°C pro-
motes partial decomposition forming LiAl₅O₈. Upon cooling,
however, γ-LiAlO₂ retains its structure at room temperature.
More recently, Mason and Van Drunen [39] have investigated
the stability and formation of β-LiAlO₂ in various carbonate
and gas environments.

A recent systematic study of the phase transformations
in a carbonate environment has been carried out at Argonne
National Laboratory [40]. The major conclusions are -

1. The presence of Li₂CO₃ either in the eutectic mix-
ture or as a solid decreased the temperature at
which either α-LiAlO₂ or β-LiAlO₂ transformed into
γ-LiAlO₂ (from 925°C to 700°C).

2. The gas environment also had an effect on the time
and temperature required for transformation:
α-LiAlO₂ transformed more readily than β-LiAlO₂ in
both air and H₂/CO₂/H₂O gas, but in pure CO₂ both
transformations occur more slowly.

An approximate phase stability diagram based on the best
judgment of all the available data is presented in Figure 2.
A more accurate thermodynamic phase stability diagram consid-
ering the gas environment, particularly CO₂/H₂O ratio, melt
composition, is needed to optimize the electrolyte support.

Structural stability (particle shape and size) is equal-
ly, or perhaps more important. α-LiAlO₂ is generally pro-
duced as a high surface area (20 to 80 m²/g) fine powder.
β-LiAlO₂ exhibits a lath habit with L/D ratios of 2 to 10.
γ-LiAlO₂ is produced as a bipyramid. For an electrolyte ma-
trix with optimum mechanical and retention properties, a mix-
ture of these structures may be desired.

A study of the structural changes in various forms of
LiAlO₂ has also been reported by Argonne National Laboratory
[40]. The following conclusions have been derived from their
work.
1. The growth of the particles was quite rapid in air, slower in CO₂.

2. The particle growth was slower in solid state than in molten carbonates.

3. The rod-shaped β-LiAlO₂ converted to low surface area bipyramids if heated at 700°C.

5. Summary

The behavior of ceramics in contact with the molten carbonates is strongly influenced by various factors, including melt composition, operating conditions and the physical form of a ceramic material. The available data should therefore be utilized with caution. Generally, in the low surface area or bulk solid forms, high density alumina, alkali aluminates, and zirconia are stable in the carbonate environment. On the other hand, silica, silicates, alumino silicates, magnesium aluminate, calcium oxide and magnesium oxide are found to be unstable. In the high surface area forms, nickel oxide and cobalt oxide show an excellent stability in oxidizing environments. High surface area alkali aluminates, particularly lithium aluminate, are promising nonconductive materials in oxidizing and reducing environments. Additional systematic study of alkali aluminate stability is required.

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Figure 1. Liquidus curves $f(T)$ for binary carbonate systems and semiempirical equilibrium composition curves $\phi(T)$ at the coexistence of corresponding aluminates [21]

Figure 2. Approximate lithium aluminate phase stability