DETERMINATION OF OPTIMUM ELECTROLYTE COMPOSITION FOR MOLTEN CARBONATE FUEL CELLS

QUARTERLY TECHNICAL PROGRESS REPORT

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Prepared By

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MASTER

NOTICE

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TITLE: DETERMINATION OF OPTIMUM ELECTROLYTE
               COMPOSITION FOR MOLTEN CARBONATE FUEL CELL

CONTRACT NO.: DE-AC21-86MC23264

CONTRACTOR: Energy Research Corp.
               3 Great Pasture Road
               Danbury, CT 06813

CONTRACT PERIOD: October 1, 1986 to September 30, 1988

OBJECTIVE: The objective of this study is to determine the
optimum electrolyte composition for molten carbonate fuel
cells. To accomplish this, the contractor will provide:

1. Comprehensive reports of on-going efforts to optimize
   carbonate composition.
2. A list of characteristics affected by electrolyte
   composition variations (e.g. ionic conductivity, vapor
   pressure, melting range, gas solubility, exchange current
   densities on NiO, corrosion and cathode dissolution
   potential:
3. Assessment of the effects these characteristics have on
   state-of-the-art cell voltage and lifetime.

CONTRACT TASKS:

Task 1. Preparation of Management Plan.
Task 2. Literature Survey to review completed and ongoing
         efforts to optimize MCFC electrolyte composition.
Task 3. Electrolyte Composition Screening to define
         "Optimum" in terms of carbonate properties and fuel
         cell parameters.
Task 4. Test Plan submission describing methods to be used
         for identifying and verifying the optimum
         composition criteria.
Task 5. Experimental Determination of Optimum Electrolytes
         by a variety of out-of-cell and in-cell tests.

TASK 1.   PREPARATION OF MANAGEMENT PLAN (completed).

TASK 2.   LITERATURE SURVEY

During this reporting period, existing information on MCFC Corrosion, Cathode Kinetics, NiO dissolution, and Lithium Aluminate stability as a function of electrolyte composition was reviewed. Additional literature information has been surveyed using the data base Molten Salt Data Center of Rensselaer Polytechnic Institute. Preliminary discussions of the quantitative criteria for composition selection are also presented.

2.1 Corrosion

Iron- and Iron/nickel based alloys (316L, 310S, Incoloy 825) are being used as current collector and bipolar plate materials in MCFC applications. Corrosion of these materials causes both increase in ohmic contact resistance and loss of electrolyte. The formation of primarily lithium-containing oxide scale changes the electrolyte composition to a lower lithium content. Hence, both endurance and initial performance of a cell or stack may be reduced. Therefore, hot corrosion is one of the important consideration in selecting an optimum electrolyte composition.

Corrosion studies in molten carbonate melt that were done prior to 1980 have been reviewed by Selman and Maru(5). The passivity of stainless steel alloys in a variety of melts including Li/Na, Li/Na/K compositions has been evaluated in static and potentiostatic testing. However, the effect of melt composition was not studied very systematically, and most of the samples tested were completely submerged in the melt. Hence most of these experiments did not adequately represent typical corrosion in an MCFC environment where only a thin film of electrolyte covers hardware and current collectors. Moreover, different gas compositions and temperatures used by various researchers in the surveyed tests make evaluation of

the effect of melt composition difficult; also some gases used, e.g. air, are not representative of MCFC oxidant.

More recent corrosion studies have been mostly carried out in 62Li/38K eutectic melt and the emphasis has been mainly on screening different alloys for MCFC application. The effect of melt composition on cell performance has been mostly studied in short-term laboratory cells with SS-316 hardware ([2]). The corrosion of these cells was not evaluated in depth because of their relatively short duration. Shores and Singh([6]) have reported more corrosion attack in a TGA experiment on SS-316L (~50 hours at 650°C) in Li/Na than in Li/K eutectic compositions. Nishikata and Haruyama([31,32]) also studied the corrosion of Fe, Ni, and Fe-Cr stainless steels in Li-Na melt at 700°C by using a potentiodynamic polarization method. However, they found that anodic dissolution current for Ni and Fe in Li/Na eutectic melt increases with <u>decreasing</u> melt basicity (i.e., by increasing p_{CO_2}). These results are in agreement with ERC's studies of NiO dissolution. Therefore, the higher melt basicity in a LiNa than in a LiK melt can probably not alone explain the greater corrosion in LiNa melts as was reported by Shores and Singh ([6]). Other factors such as mass transfer resistance in the scale and differences in oxy-anion (O_2^-, $O_2^=$) concentrations may also affect the hot corrosion rate.

Recent results at ERC have shown that MgO as an additive for suppressing NiO dissolution, although it increases melt basicity, did not cause significantly more corrosion of 310S or 316L current collectors. Because no clear conclusions are presently available from literature sources, a more systematic study in a well-defined environment is clearly required to understand the effect of melt composition on hot corrosion.

● <u>Electrolyte Selection Criteria With Respect to Corrosion</u>

Based on recent corrosion studies by GE[7] and ERC[8], high Cr-Ni alloys (e.g., 310S) show generally better corrosion resistance than the lower Cr-Ni alloys (e.g. 316L). Nishikata and Haruyama [31,32] studied the corrosion of Fe-Cr stainless steels in Li/Na melt and found that a high Cr content improved hot corrosion resistance. The high Cr content promotes formation of a compact Cr-rich passive layer in oxidant atmosphere and buffers the melt basicity by $CrO_4^=$ formation. Thus, the higher Cr-Ni content of 310S may be able to combat the possibly more corrosive environment of a melt. Accordingly, in this study 310S (25Cr-20Ni-Bal.Fe) will probably be used as the alloy for studying melt composition effects in terms of corrosion behavior.

A corrosion rate of 50 $\mu m/(yr)^{1/2}$ appears acceptable in the range of 25,000 to 40,000 hours. This value, is suggested as one of the selection criteria for electrolyte screening. Any electrolyte composition causing more than 50 $\mu m/(yr)^{1/2}$ corrosion attack on 310S alloy in a standard environment should be derated, as this implies that about half the thickness of a 250 μm bipolar sheet may be lost in 4 years. Another corrosion selection criterion that could be given some importance should be the ohmic resistance of the passive oxide layers formed on an alloy. This clearly is related to the already mentioned thickness of the layers, but also introduces the specific bulk resistance (σ) of the passivating oxide film. The value of σ may vary as a function of cation concentration and hence electrolyte composition.

High basicity melts will be preferred because of the expected lower NiO solubility provided their corrosion rate is acceptable. A system of weighting the quantitative screening criteria at the primary and secondary levels in our selection process will be introduced in an upcoming topical report on this subject.
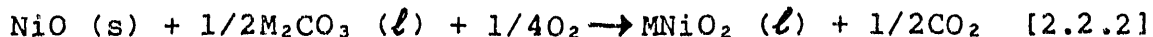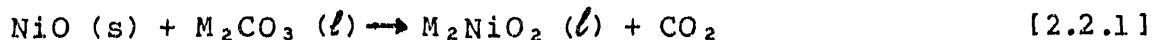
2.2   NiO Dissolution

In-situ oxidized, porous, lithiated nickel oxide has been used as the standard cathode structure for many years. Although NiO has an equilibrium solubility in carbonate melts of only a few parts per million, the dissolved nickel ions generally diffuse toward the anode as a result of a source-to-sink concentration gradient. At some point, dissolved Ni ions reprecipitate as Ni metal when they meet more reducing conditions, probably caused by dissolved hydrogen in the melt. Because this again removes nickel ions from solution, further cathode loss can occur by Ni-ion transport.

ERC has found that cathodes may lose up to 30 to 40% of their total mass in nickel and still function within the desired performance limits(9). However, because such a loss often occurs in approximately one year, the cathode would be completely dissolved by 25,000 hours of life. Additionally, the measured dissolution rate of ~6 μm/hr.cm^2 (as measured in some of our cells lasting up to 10,000 hours with 62LI/38K electrolyte) also appears to be linear with no sign of a decrease in rate.

2.2.1   Dissolution Mechanisms

NiO is an amphoteric material, dissolving as an acid in a basic melt and as a base in an acidic melt. Four cases are possible; viz basic and acidic, and dissolution as the reduced or oxidized species. The chemical reactions are:

Basic Dissolution

$$NiO\ (s) + M_2CO_3\ (\ell) \rightarrow M_2NiO_2\ (\ell) + CO_2 \qquad [2.2.1]$$

$$NiO\ (s) + 1/2M_2CO_3\ (\ell) + 1/4O_2 \rightarrow MNiO_2\ (\ell) + 1/2CO_2 \qquad [2.2.2]$$

Acidic Dissolution

$$NiO\ (s) + CO_2 \rightarrow Ni^{2+} + CO_3^= \qquad [2.2.3]$$

$$2NiO\ (s) + 3CO_2 + 1/2O_2 \rightarrow 2Ni^{3+} + 3\ CO_3^= \qquad [2.2.4]$$
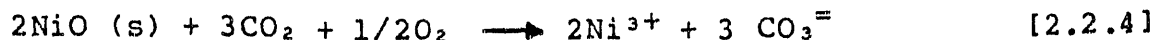
Acidic dissolution of Ni(II) has been shown to predominate under MCFC cathode conditions [24-28]. $NiO_2^=$ concentration was considered negligible by Vogel et al.[24]. However, Remick [28] proposed the existence of $NiO_2^=$ in Li/K melt based on the solubility measurements of Orfield and Shores[29-30] at $910^{\circ}C$. Doyon, et al.[27] have found that the basic dissolution in Li/K melt at $650^{\circ}C$ cannot be explained solely by Equations [2.2.1] or [2.2.2], although it is possible that $NiO_2^=$ or NiO_2^- can coexist in molten carbonate under varying cathodic conditions.

In summary, most published results agree upon the predominance of acidic dissolution of Ni(II) in $(Li/K)CO_3$ melts under MCFC oxidant conditions. And the equilibrium solubility in a generally standard oxidant/electrolyte environment is approximately 10 ppm by weight as Ni. ERC began its studies of the effect of different fuel cell environments on NiO solubility[10] by modifying the acid/base character of the melt. Equilibrium solubility was later also correlated with the NiO loss rate measured in a number of cell tests[11].

Effect of Gas Composition: Because the acidic dissolution [Eq. 2.2.3] predominates in Li/K melts at $650^{\circ}C$, it is expected that a higher partial pressure of CO_2, which makes the melt more acidic, promotes NiO dissolution. This phenomenon has been confirmed experimentally by various researchers[10,25-28]. A short tabulation of average ERC data is shown below:

Vol. % CO_2	Solubility as Ni, ppm
10	4
25	10
85	21

This clearly supports the acid dissolution reaction even though the measurement of these very small nickel concentrations in carbonate melt is a very difficult analysis (i.e., reproducibility at ± 2 ppm).

Effect of Electrolyte Composition: A change in the elemental composition of the melt can have a significant effect on the melt's acid/base character, and hence influence nickel solubility. Normally, any of the constituent alkali cations, even though the melt is almost completely ionized, can also combine and dissociate according to the type reaction given in Equation 2.2.5 with a dissociation constant as shown in Equation 2.2.6 (M = alkali cations):

$$M_2CO_3 \longrightarrow M_2O + CO_2 \qquad\qquad [2.2.5]$$

$$K = \frac{a_{M_2O} \cdot P_{CO_2}}{a_{M_2CO_3}} \qquad\qquad [2.2.6]$$

In terms of acidic dissolution [e.g. Equation 2.2.3], it is clear from the above that another simultaneous reaction occurs [Equation 2.2.5] which affects the CO_2 content and therefore the acid/base character of the melt. Because as a given alkali oxide content increases, resulting in less dissolved CO_2 for a given K, the solubility of NiO will decrease simultaneously. In other words, basicity is also buffered by the type and concentration of the alkali metal ion content. For a constant CO_2 partial pressure, the overall dissociation constant of the carbonate melt will also change depending on the activity (i.e. cation type) of alkali ion content. It is known([12]) that the order of the dissociation magnitudes (i.e. Equation 2.2.5) of the different alkali carbonates is Li > Na > K. It can be implied from this that an increase in concentration of the more basic buffering lithium carbonate constituent of a carbonate melt, or change to an equal ratio Li/Na

mixture, should increase alkalinity and decrease the solubility of NiO.

Orfield and Shores[29] determined the solubility of NiO at 910°C in six different binary mixtures of Li/K carbonate. In general, their data do show that with higher Li content, (i.e. a more alkaline nature of the melt), there is somewhat lower NiO solubility, except that over the range from 50Li/50K to 85Li/15K molar ratios, NiO solubility is virtually unchanged. On the other hand, Baumgartner's data [25,26] showed an increasing NiO solubility with increasing lithium mole fraction at 900°C. However, this discrepancy may have been caused by the difference in the H_2O content in the gases used in these high temperature experiments; Baumgartner used 3.1% H_2O while Orfield and Shores used dry gas. Extrapolation of Baumgartner's data to 650°C has shown that NiO dissolution increases in the sequence of 75Li/25K >35Li/65K >50Li/50K >62Li/38K, although the differences are not very significant. Thus it appears that NiO dissolution is definitely a function of melt basicity as well as the nature of the melt. No extrapolation of Orfield and Shores' data is possible because the effect of temperature was not studied.

Recently at ERC, the use of 75 mole% lithium in comparison to 62% lithium carbonate has been shown to decrease Ni solubility from 9 to 3 ppm[10]. Moreover, this was true even when 10% water vapor was present. Similarly, substitution of the more basic sodium carbonate for potassium carbonate also has decreased the solubility of NiO in several experiments to an average of 4 ppm[13]. Recent cell testing by IGT[28] has also shown that NiO dissolution increases with decreasing Li content in Li/K melts which is in agreement with ERC's findings. Therefore it appears that up to a point, the higher the melt basicity, the lower will be the NiO solubility. Although from the existing data it is clear that the effects

of alkali composition of the melt (e.g. Li vs. Na vs. K cations) and the H_2O content should be further and more systematically examined.

Effect of Temperature: According to Baumgartner[25,26], the higher the temperature, the higher the NiO solubility in Li/K melts. However, the opposite results were reported by Ota et al.[40]. Therefore, if a different MCFC operating temperature, other than 650°C is selected, this inconsistency should be resolved.

● Electrolyte Selection Criteria With Respect to NiO Dissolution

As shown in Figure 2.2.1, it has been demonstrated at ERC[13] that an apparently linear correlation exists between equilibrium solubility measured in out-of-cell solubility tests and the loss of Ni from cathodes that were operated in cells for specific periods of time and under different oxidant conditions and with different electrolyte compositions. A loss rate goal can thus be estimated which will achieve a loss of less than the 40% tolerable weight decrease of a cathode over 25,000 hours of operation. This has been calculated to be approximately <3.5 $\mu g/hr.cm^2$ of Ni per cell geometric area in cm^2. A number of cells have been run which are beginning to approach this goal, as shown below:

Cell No.	Loss rate $\mu g/hr.cm^2$	Average Conditions
7-93	3.6	13% CO_2 in 62Li/38K carbonate
7-89	3.6	53Li/47Na electrolyte with 25% CO_2
7-90	2.6	<10% CO_2 with 62Li/38K electrolyte

Thus, it is clear that in the context of the present electrolyte composition study, there is good potential for decreasing the Ni-loss rate by lowering its solubility as a result of further changes in electrolyte acid/base equili-
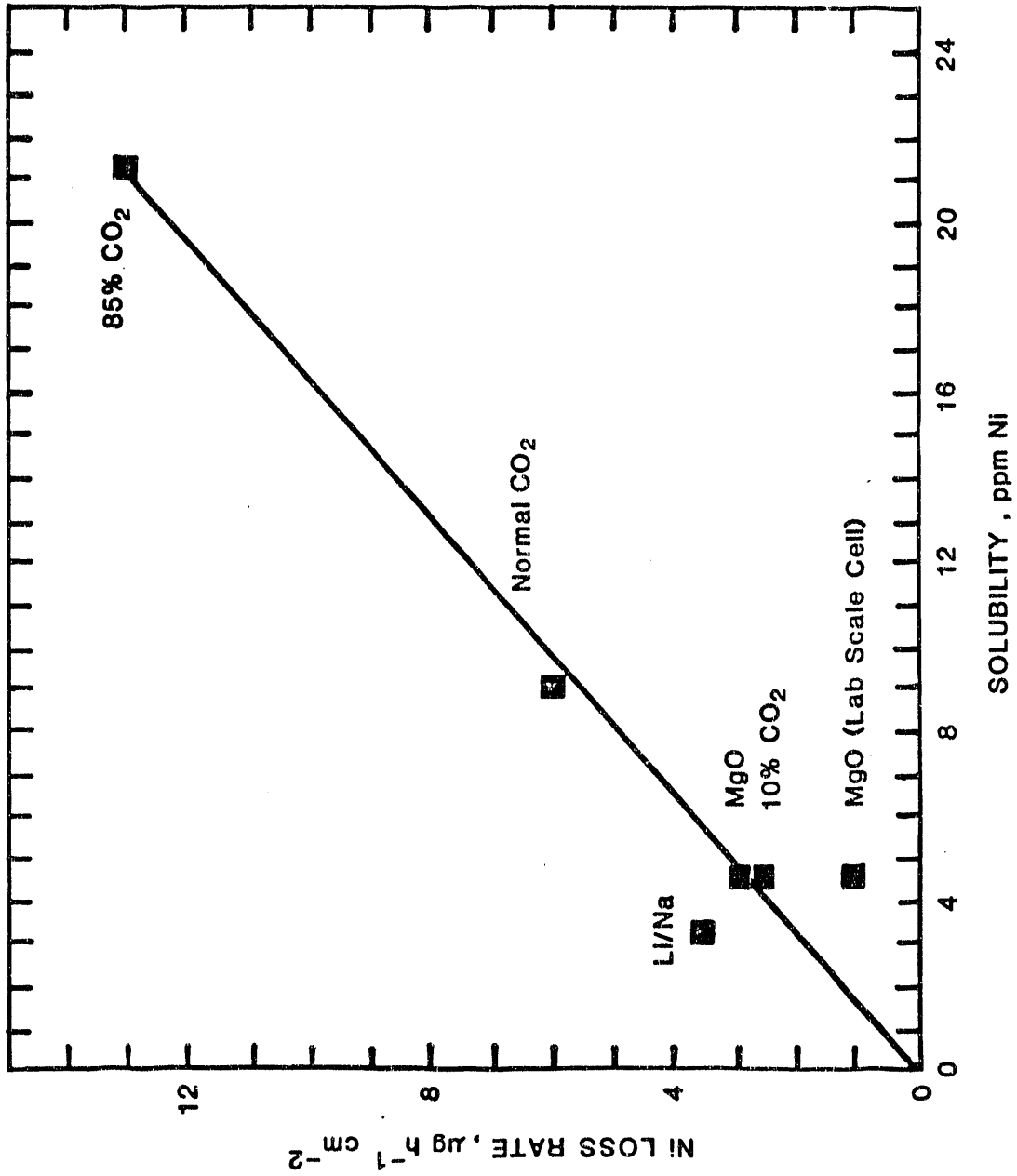
Figure 2.2.1   CORRELATION OF Ni LOSS RATE IN CELL OPERATION
                WITH EQUILIBRIUM SOLUBILITY OF Ni

brium. The criterion of $3.5 \mu g/hr.cm^2$ calculated to be a reasonable loss rate goal correlates with a solubility of ~5 ppm of Ni in the electrolyte.

2.3 Cathode Kinetics

The currently used NiO cathode structure contributes significantly to the polarization of an MCFC because, comparing the two 1/2-cell reactions, the cathode oxygen reduction step tends to be the slowest of the kinetic processess. The selection of melt composition to improve cathode kinetics therefore becomes an important issue. Cathode kinetic studies prior to 1980 were also reviewed by Selman and Maru[5]. Sophisticated early investigations were those of Appleby and Nicholson[14] using a potential sweep method. The key factor in their work was the identification of O_2^- and $O_2^=$ peroxide ion occuring during the oxygen reduction reaction. Exchange current densities (i^0) were estimated from their data and it appeared that the sequence of the i^0 magnitude is Li/K > Li > Na/K. However, compared to later work, their technique greatly underestimated the magnitude of these exchange current densities as was also pointed out by Lu[15]. Hence this ranking in terms of i^0 has to be viewed with caution.

A review of recent research on kinetics[16] has shown that a consistent description of the steps occuring in the cathode reaction mechanism is still not available. Many conflicting results have been reported and the kinetic parameters cannot be completely explained. Uchida and coworkers[17,18] also have studied electrokinetic parameters in different carbonate melts (e.g. Li/K, Li/Na, Na/K, and Li/Na/K) using a potential sweep technique at 750^0C. They found that the more acidic the melt is (e.g. 43Li/57K compared to 43.5Li/31.5Na/25K), the higher the peak current (i_p). This implies a higher solubility or diffusivity of active species (peroxide, superoxide, etc.) in the more acidic melt (a K-rich melt), as was also previously pointed out[2]. Additionally,

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the exchange current density for oxygen reduction may also
have been higher in the more acidic melt (i.e. 43Li/57K), but
this could not be confirmed by the potential sweep technique
due to the high reversibility of the molten carbonate cathode
system.

Lu([15]) has determined the i^O on Au in a 62Li/38K melt by
a potential step (PS) method and found it to be ~11 mA/cm².
This value is considerably higher than those estimated by
Appleby and Nicholson([14,20]). However, Lu's findings were
independently confirmed by Uchida's results ([21,22]) in the
43Li/57K melt. Uchida utilized the AC-impedance and also
Coulostatic relaxation (CS) methods to study the kinetics in
this low lithium, eutectic composition and found i_O to be
between 20 and 40 mA/cm² both on Au and on NiO. These numbers
are only slightly higher than those determined by the PS
method used by Lu. Uchida, et al.([18]) have also measured i_O
in other Li/K melts by the Coulostatic relaxation method and
found the magnitude to follow the sequence 43Li/57K > 35Li/65K
> 49Li/51K > 62Li/38K. Although not entirely consistent, this
ranking does appear to show, from a kinetic point of view,
that the more acidic melts are more attractive.

McCoy and Schuman([41]) have used a gold rotating disk
electrode to study cathode kinetics in a Li/K eutectic melt.
It was found that the carbonate system is much more compli-
cated than originally thoughtand the active species were not
clearly identified. In addition to the peroxide and super-
oxide ions, other species may also be involved in the cathode
reaction. According to the peroxide/superoxide mechanism
proposed by Appleby and Nicholson([5,20]), the exchange current
density of the cathode reaction may be expressed as:

$$i_O = i_O^O \cdot (O_2^- \text{ or } O_2^=)p \cdot (O^=)q \qquad [2.3.1]$$

where i_O^O is the standard exchange current density, and p and q

are reaction constants. The concentrations of the various
species, O_2^-, $O_2^=$, and $O^=$, and the i_O^O values are all functions
of melt composition.

Thus basicity, which is mostly related to $(O^=)$, is only
partly responsible for the value of i_O. Furthermore, Appleby
and Nicholson[5,20] proposed that both peroxide and superoxide
ions exist in the carbonate melt but could become reduced to
oxide ion on the MCFC cathode surface, as was confirmed by
Harada et al.[33] in a Na/K melt. All these theoretical
considerations clearly indicate that many factors in addition
to melt basicity affect cathode kinetics and a systematic
study is very much needed.

Other researchers have studied molten carbonate kinetics
on porous NiO cathodes[23], but only the 62Li/38K melt was
used and hence the effect of melt composition is not avail-
able. Furthermore, only the steady-state technique was used
in the above referenced work by Tang. This technique, how-
ever, cannot separate the pure electrode kinetics from overall
cell impedance. Mathematical modeling of such steady-state
data has, of course, been used to discern the different resis-
tances involved. However, the method not only has difficulty
in predicting cathode performance but also results in doubtful
kinetic parameters.

From the above discussion it appears that a potassium-
rich melt, because it is more acidic, may promote cathode
kinetics possibly also due to somewhat higher gas solubili-
ties. But, as mentioned, our literature search primarily
indicates that a detailed mechanism for MCFC cathode kinetics
which could identify the importance of such gas solubility is
still not available. This is because present empirical para-
meters cannot explain the possible theoretical mechanisms that
have been advanced. Furthermore, it appears from the actual
cell data reviewed in our last quarterly report, that a high

melt conductivity (e.g. Li/Na) may improve cell performance despite the cathode being kinetically less favored in such a less acidic environment.

Finally, prediction of porous electrode performance from fundamental properties obtained in <u>deep melt</u> experiments has always posed enormous difficulties due to: 1) the complex nature of the 3-phase interface at the active reaction sites; 2) the effective porous conductivity of the electrode and; 3) the difference between mass transfer in completely flooded pores compared to that in a partially gas, partially liquid filled structure. Recently, Yuh([16]) has used an AC-impedance technique to study the kinetics and mass transfer resistance of a NiO porous electrode as oxidized <u>in-situ</u> and operated as a partially flooded cathode; however, again, only the 62Li/38K melt was used.

Nevertheless, The AC-impedance method will be capable of separating kinetic from mass transfer impedances while they are being directly measured in a porous partially filled electrode. Both the reaction orders and the activation energies of the oxygen reduction reaction can be extracted. Therefore, this is clearly a powerful technique because both kinetic (i.e. activation polarization parameters) and mass transfer (i.e. concentration polarization parameters) are being directly measured in a realistic porous electrode environment under actual fuel cell conditions. This cannot be done in any deep-melt, electrochemical experiment. And even if only relative information with respect to electrolyte composition can be obtained with the AC-impedance technique, it is expected that this will directly apply to in-cell cathode performance and therefore be very useful for comparative screening of different carbonate melts.

The importance of the conductivity of the electrolyte itself in cathode performance may be realized by the fact that a NiO porous electrode represents a distributed parameter system. The effective electrolyte conductivity in this system, in addition to i_o may strongly affect the overall cathode performance under certain conditions, as was already pointed by Yuh[16].

●   Electrolyte Selection Criteria With Respect To Cathode Kinetics

In this screening effort relevant to cathode kinetics and electrode mass transfer, the AC-impedance parameters will be obtained on a porous, in-situ oxidized, NiO cathode at 650°C. Three different electrolyte compositions selected from the 5 original compositions will be used (i.e. as screened by Corrosion and NiO dissolution experiments). One of the criteria for electrolyte selection as a function of electrode kinetics tentatively has been decided to be porous cathode, impedance of <0.9 $\Omega.cm^2$ ($\sim$145 mV cathode polarization at 160 mA/cm^2). The electrolyte composition showing the lowest total impedance below this figure will be the highest rated in this selection category. However, separate kinetic and mass transfer contributions which will be obtained by the AC-impedance technique must also be considered before a final optimum composition is selected.

2.4   Lithium Aluminate Stability

Lithium aluminate is prepared from various lithium and alumina sources and exists in 3 allotropic forms at MCFC temperatures:

●   hexagonal, α-LiAlO$_2$ with mostly spherical particles;

●   orthorhombic β-LiAlO$_2$ of acicular form;

●   and tetragonal γ-LiAlO$_2$ with bipyramidal particles.

There are two primary aspects to $LiAlO_2$ stability in a molten carbonate fuel cell matrix: 1) the growth in number and size of large crystallites at the expense of very fine particles with an attendant loss of surface area (i.e., due to an Ostwald ripening or dissolution/precipitation mechanism) and, 2) transformation of the $LiAlO_2$ crystal structures with a consequent increase in bulk volume (e.g. 0.294 cc/g α-phase may transform to 0.382 cc/g γ-phase[4,1]). These various morphological size and structural changes resulting from intimate contact between $LiAlO_2$ matrix particles in an MCFC electrolyte environment at $650^{\circ}C$ were studied at ERC in a number of pot tests (2000 hours) and have been regularly documented as they occured in bench-scale cell tests.

However, the stability effects of only two Li/K compositions on various combinations of the $LiAlO_2$ allotropes were studied in some depth[4]. Although some inconsistencies were encountered, the general observations were that mean particle size growth from 0.3 to >10 μm could occasionally be observed in 2000 hours. This occurs more frequently when the starting material is α- or β-phase transforming to γ-phase, while the attendant BET surface area changes are from approximately 15 to 25 m^2/g decreasing to <5 m^2/g.

The γ-allotrope was unquestionably the most stable form of $LiAlO_2$ in all electrolyte compositions because all tests between $650^{\circ}C$ and $750^{\circ}C$ showed that the γ-concentration either grew or remained at a very high level if the original powder was primarily γ-$LiAlO_2$; if the original powder had a high α- or β- content, the concentration of these allotropes always became much lower at the end of 2000 hours. This is the same conclusion reached by numerous other workers as quoted in earlier surveys[1,5] who have also stated that the eventual complete and irreversible transformation to γ-$LiAlO_2$ occurs in the range of 600° to $750^{\circ}C$ at normal pressures. Furthermore, the effect of lower melt alkalinity (higher P_{CO_2}) on surface

area retention of γ-LiAlO$_2$ was studied in equivalent 62Li/38K electrolyte compositions; it was shown that there is somewhat better BET surface area retention in more acidic environments. Also, the effect of accelerated sintering at 700°C compared to 650°C appeared to be minimal with γ-LiAlO$_2$ material. However. particle growth was always greater with materials high in α- and β-phase LiAlO$_2$. Thus, the greater stability characteristics of γ-LiAlO$_2$ have so far made it the material of choice as matrix support for most carbonate electrolyte compositions.

Broers and van Ballegoy[43] some years ago also presented thermodynamic data and determined a phase diagram for the stable regions of various alkali aluminates in different alkali carbonate melts. As shown by this diagram in Figure 2.4.1. the stability of LiAlO$_2$ versus Na or KAlO$_2$ in alkali carbonates at MCFC temperature, independent of crystal structure, is very high when the melt contains at least 25 mol% Li$_2$CO$_3$. This early contribution to MCFC technology also stated that alkali aluminates are practically insoluble in most carbonate melts; e.g., the solubility of LiAlO$_2$ in the ternary eutectic melt at 700°C was estimated at ~10 ppm (mole/mole of carbonate).

In general. the possible changes in particle size and shape due to sintering and structural expansion of the ceramic phase can have an impact on the overall porosity and pore size distribution as well as particle-to-particle contact in the matrix. This changes both matrix capillarity and bulk strength with consequent effects on the distribution of electrolyte between matrix and electrodes and the possibility of cross leakage of gases due to matrix cracking; this is of special concern when major forces from thermal cycling are brought into play.
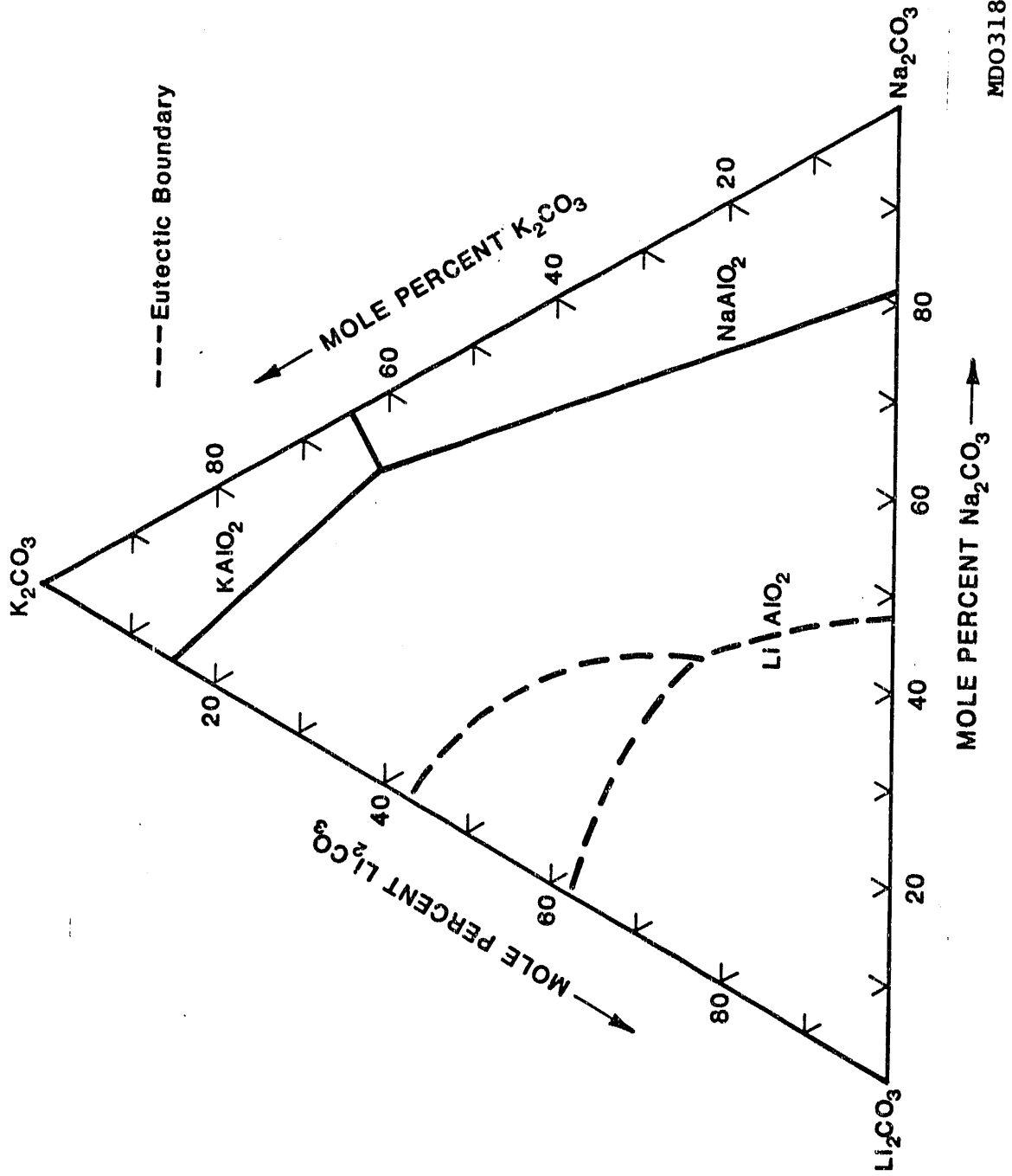
FIGURE 2.4.1 STABLE ALUMINATE PHASES IN THE Li_2CO_3-Na_2CO_3-K_2CO_3 SYSTEM AT 1000°K, (43)

● <u>Electrolyte Selection Criteria With Respect To Lithium Aluminate Stability</u>

A great deal of work has been done over the years to manufacture as stable a matrix composition as possible. This has been achieved largely through a process of blending various mixtures of high and low surface area powders interspersed with crack arrestors, bolders and/or filamentory structures. However, some phenomena of coarsening and allotrope transformation continue to be observed and should be evaluated, particularly as no rigorous experimental data are available for an entirely new, possibly sodium containing melt.

On the whole, it is clear that the chemical composition of $LiAlO_2$ can be expected to be stable in most candidate alkali-electrolyte compositions while its labile allotrope structure will still irreversibly tend toward γ-$LiAlO_2$. Starting with a powder of predominately this crystal phase will therefore provide a minimum of breakup of crystallites which could enhance further particle growth. However, no results are available with regard to matrix coarsening as a result of dissolution/precipitation in different cation compositions or in different acid/base equilibria due to various gas atmospheres. Hence, the morphological stability of $LiAlO_2$ may not be a major problem but it deserves to be further investigated.

Using, a very fine, >95% γ-$LiAlO_2$ powder, it is suggested that different electrolyte compositions are screened in carbonate filled tape form and that the criteria of particle growth and matrix allotrope changes be as follows:

	In Original Tape	Changes after 3000 hours no greater than
325-Screened		
Particle size, μm	2 to 6	6 to 10
Mean Pore Size, μm	0.1	0.5
BET Surface Area, m^2/g	7 - 10	~5
γ-LiAlO$_2$	>95%	>95%

2.5 Electrolyte Conductivity

As discussed in our previous quarterly progress report, cells with higher conductivity electrolytes have lower total cell resistance and may have better performance. The higher cell performance may be due in part to the smaller contributions of ohmic resistance in both the matrix and in the porous electrodes but many other variables also enter into the over-all performance of a cell. The most recent extensive review of electrolyte conductivity in binary and ternary carbonate melts has been given by Selman and Maru[5]. During this reporting period, new data obtained from the Molten Salt Data Center at RPI were reviewed. Figure 2.5.1a shows the electrolyte conductivity of (60Li/40K)CO$_3$ measured by various research groups[34-36]. The results are all of the same order of magnitude and agree quite well over the years with the most recent contribution by Tanase[34] in Japan.

The conductivities versus various Li contents are illustrated in Figure 2.5.1b. The effect of Li mole% in Li/K and Li/Na melts is shown next as calculated from correlated Arrhenius-type equations supplied by Tanase. This figure clearly shows the almost two-fold higher electrolyte conductivity of Li/Na carbonate compared to Li/K melts. And in both cases going to higher Li content, there is a steep rise toward better electrolyte conductivity. Based on these latest electrolyte conductivity data, it appears that a Li-rich, sodium-containing melt could be an important improvement over the standard Li/K melts as was also found in earlier cell tests.
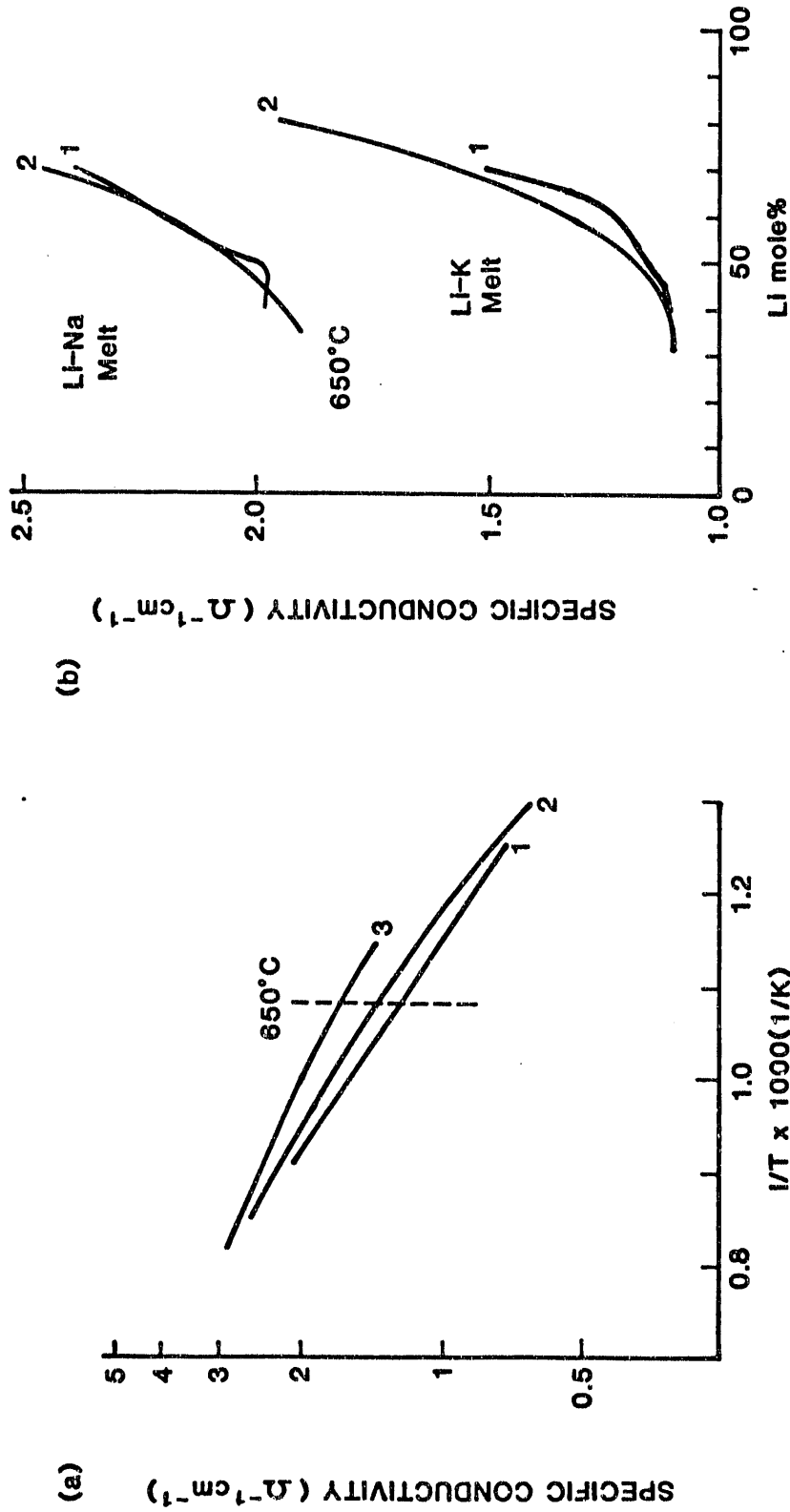
Figure 2.5.1 (a) Electrolyte Conductivity of Binary (60 mole % Li$_2$CO$_3$ –40 mole % K$_2$CO$_3$) Melt.

(b) Effect of Li mole % on Electrolyte Conductivity

[1–Tanase et al.(34); 2–Vorob'ev et al.(35); 3–Spedding(36)]

In terms of ternary melt data, those measured by Ward and Janz[39], and Noda, et. al.[38] were compared with the data of Pal'guev and Vorob'ev[37]. The comparison shows that the data of Ward and Janz[39] are close to those of Pal'guev and Vorob'ev[37] whereas the data measured by Noda et. al. are not. But, because only limited ternary data are available so far, no rigorous cross checks of these results with measurements by Pal'guev and Vorob'ev are possible. Nevertheless, a similar trend as in Li/K and Li/Na binary melts is indicated and also the higher the Li content, the higher is the melt conductivity.

- ## Electrolyte Selection Criteria With Respect to Electrolyte Conductivity

Because a cell's IR loss is a major part of the total performance loss and IR is strongly affected by electrolyte conductivity, electrolyte compositions with higher conductivities are clearly preferred. Additionally, higher electrolyte conductivity may also play an important part in improving cathode kinetics. The currently used 62Li/38K carbonate melt has a conductivity of approximately 1.4 $(\Omega.cm)^{-1}$ at $650^{\circ}C$. This conductivity value is tentatively selected as the quantitative selection criterion which must be significantly exceeded for a new electrolyte composition to be selected.

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