

DETERMINATION OF OPTIMUM ELECTROLYTE COMPOSITION
FOR MOLTEN CARBONATE FUEL CELLS

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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
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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 effects.
3. Assessment of the overall effects that 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.

PROGRESS BY TASK

TASK 2 LITERATURE SURVEY

During this quarter, further articles in connection with electrolyte composition effects were reviewed. Lee and Shores (73,74) studied corrosion of nickel and nickel-chromium alloys in molten carbonate at 650°C. They suggest that the hot melt corrosion of nickel or nickel-chromium alloys in O₂-CO₂ atmosphere is initiated by basic fluxing of NiO₂²⁻. The reaction of Cr₂O₃, formed on Ni-Cr alloys, with molten carbonate to form chromite and chromate compounds can significantly change melt basicity and composition and therefore influence hot corrosion rate. They suggest that this fast formation of chromate or even chromite on nickel-chromium alloys results in protective or non-protective scale formation, respectively.

The same theoretical analysis with some modifications may also be applied to corrosion of iron-base stainless 'steels' (310S or 316L, etc.) in molten carbonate. In a cathodic oxidizing atmosphere, Fe₂O₃ and Cr₂O₃ first form on stainless steels. However, the Fe₂O₃ reacts with Li₂CO₃ to form LiFeO₂, which is only slightly soluble in molten carbonate (72). Cr₂O₃ also reacts with molten carbonate to form highly soluble chromate (72), as in the nickel-chromium system. The above reactions change the melt composition near the surface to a K-rich, chromate-containing melt.

According to Hsu and Devan (72), the slight equilibrium solubility of LiFeO₂ is independent of melt basicity in an oxidizing atmosphere. And therefore, the change in melt basicity as a result of melt compositional changes may not significantly affect the rate of attack due to fluxing, in line with ERC's finding in the present program. It has been found that different candidate melt compositions do not appear to affect corrosion of 310S in oxidant atmosphere. On the other hand, the change in melt composition resulting

from ferrite and chromate formation may change the 'melting' point to such an extent that the electrolyte film may become solidified and does not participate in a fluxing attack.

In conclusion, the formation of a passivating $\text{LiFeO}_2 + \text{Cr}_2\text{O}_3$ oxide layer on 310S stainless steel may result from the fast formation and dissolution of chromate, as in Ni-Cr systems. The little effect of melt basicity on the solubility of LiFeO_2 may explain why there is little effect of melt composition on the compact Cr_2O_3 passivating layer underneath and therefore on hot corrosion of 310S in molten carbonates. However, in the anode atmosphere, a fast formation of the chromite salt, LiCrO_2 , and the formation of other ferrites (e.g. LiFeO_5O_8 or $\text{Li}_2\text{Fe}_3\text{O}_5$) other than the low solubility LiFeO_2 may explain the fast corrosion of stainless steels in molten carbonates. The solubility of the LiFe_5O_8 or $\text{Li}_2\text{Fe}_3\text{O}_5$ in the anode atmosphere should be studied in order to clarify this corrosion mechanisms.

New articles in connection with electrolyte composition effects on NiO solubility were also reviewed. Lee (74) in his recent thesis has reported solubilities of NiO in Li/K mixtures at 650°C . His results indicate a strong effect of Li-content on the equilibrium solubility of NiO; increasing lithium content reduces the solubility, in agreement with the results reported in the general literature. This is also the primary reason that Li-rich off-eutectics in the Li/Na and Li/K systems were chosen as the candidate electrolytes to be optimized. Lee's results also show that the NiO solubility in Li/K melt is linearly proportional to the K_2CO_3 mole fraction in the compositional range from 20 to 65% K_2CO_3 . But, because the melt acidity is unlikely to vary linearly with respect to the more alkaline Li_2CO_3 mole fraction in a Li/K binary mixture, the acidic solubility is not a single-valued linear function of the acidity (or basicity). Therefore the NiO solubility depends also on the nature of the second and/or third components in a mixture.

The solubility of NiO in 62Li/38K melt at 85% CO₂, measured by Lee (74), is approximately 22 wt. ppm, nearly equal to ERC's finding (~20 wt. ppm). Therefore, our results are further confirmed. However, his log [NiO solubility] vs. log [P_{CO₂}] plot indicates an acidic slope of ~0.3, which is much less than the theoretical slope of 1.0 if NiO + CO₂ ⇌ Ni⁺⁺ + CO₃⁻ is the dissolution reaction. Moreover, this theoretical acidic slope of 1.0 was confirmed by Doyon, et al (75). The discrepancy may be caused by the difference in analytical procedures used in the very low solubility ranges (<5 wt. ppm). Doyon, et. al (75) used an ICP Atomic-Emission Spectroscopic technique to determine Ni concentration (as was also used in this program) which is felt to be more accurate than the colorimetric method used by Lee (74). Furthermore, a pressurized high CO₂-content gas atmosphere (up to 9 atm) employed by Doyon et al. allows for a wider range of acidic conditions to establish the experimental slope.

TASK 3 ELECTROLYTE COMPOSITION PROPERTIES

NiO solubility recently measured by D. Shores at 650°C in 62Li/38K carbonate under dry, 75% CO₂ (25% O₂) gas atmosphere is 45 ppm in mol. fraction (~27 wppm) under these conditions. This agrees only roughly with ERC's recent values of 20 wppm and with Lee's early thesis value of 22 ppm in 62Li/38K electrolyte. However, our data were obtained with an 85% CO₂ (10% O₂ + 5% H₂O) atmosphere, showing that despite the higher pCO₂ employed in this present study, less nickel was found to dissolve. This discrepancy may, however, be explained by the buffering action of the 5% H₂O that was used in the ERC measurements. If dissolved CO₂ (l) plus carbonate anion are considered the complementary strong acid components of a molten carbonate system and dissolved H₂O (l) plus alkaline hydroxide ions are the complementary weak base

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components, then an analogy with strong-acid/weak-base buffering can be made as shown in the tabulation of reactions in Table 1.

The two major differences between a molten carbonate and an aqueous system are that the highly dissociated, weak-base/strong-acid salt is also the solvent in the molten carbonate system, while water (the source of acid/base species for both systems) is only a very slightly soluble species in the high temperature carbonate melt (76). However, neither of these differences will impede the ready formation of all the required ionic or metal hydroxide species to achieve the acid buffering action.

The extremely small, high temperature solubility of unreacted water in a molten carbonate system (i.e. not measurable according to Broers) probably stems from the non-ideal mixing of free water in the hot carbonate melt. This would lead to a very weak Henry's Law dependance of $[H_2O(l)]$ on p_{H_2O} vapor pressure. There is, however, no barrier to the dissociation of the dissolved water and its reaction with carbonate to supply acid (CO_2) and base (OH^-) species from the continuous replenishing source of water vapor which may exist in the gas phase; i.e. $H_2O(g) \rightarrow H_2O(l)$ followed by $H_2O(l) + CO_3^{2-} \rightarrow CO_2 + 2 OH^-$. And thus a considerable concentration of OH^- ion can and appears to have been measured by Broers as a normal constituent of electrolyte melts in humid environment.

It has never been shown that alkali hydroxides, producing $M^+ + OH^-$ ions, are a weakly dissociating species in molten carbonate but this is unimportant as long as it is clear that a continuous replenishment of hydroxide is available to achieve some constant concentration of the buffering species (i.e. OH^- ion). The origin of the hydroxide in the molten carbonate case is of course the inexhaustible source of humidity (if present) in the gas atmosphere. Calling the MOH species a weak-base therefore is merely a device to draw

Table 1

COMPARISON OF AQUEOUS-SALT WITH MOLTEN-CARBONATE BUFFERING

(Formation of poorly dissociated hydroxides provide buffering action)

● <u>Aqueous Buffering:</u>			
$Al^{3+} + 3Cl^{-}$	+	$3H_2O$	\rightleftharpoons $Al(OH)_3(c) + 3H^{+} + 3Cl^{-}$
WEAK BASE/STRONG ACID SALT		ionizable solvent	WEAK BASE continuous replenishing_source of OH ⁻ ions STRONG ACID
● <u>Molten Carbonate Buffering:</u>			
$2M^{+} + CO_3^{=}$	+	$H_2O(l)$	\rightleftharpoons $2MOH(l) + CO_2(l)$
WEAK BASE/STRONG ACID SALT (also solvent)		continuous replenishing_source of OH ⁻ ions	WEAK BASE ? STRONG ACID
● <u>No Buffering in Absence of H₂O</u>			
$2M^{+} + CO_3^{=}$		\rightleftharpoons	$M_2O + CO_2(l)$
			very low activity

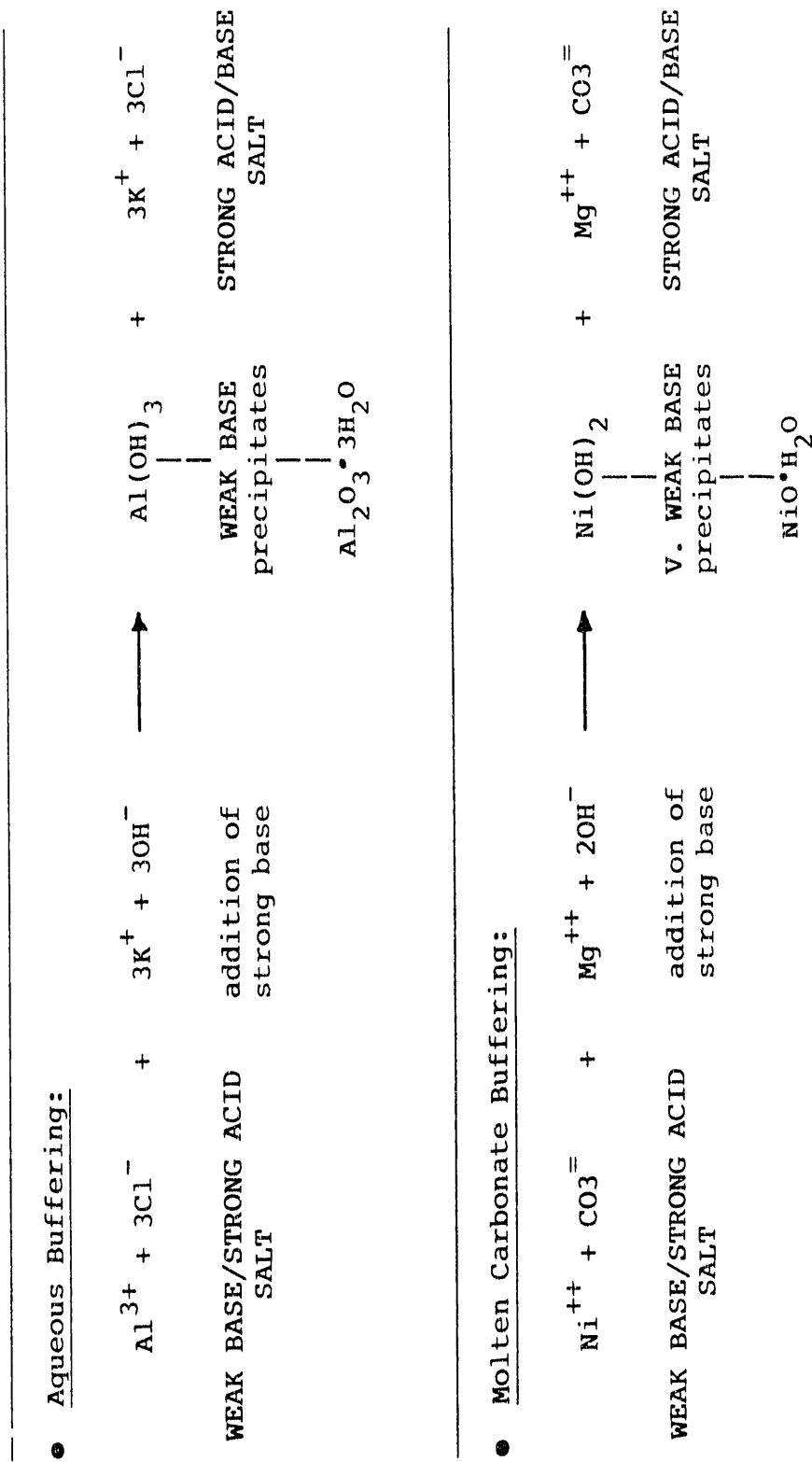
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the analogy with the concept of a large supply of readily dissociable hydroxide which will automatically buffer any addition of excess acid. In the aqueous case, it is the $\text{Al}(\text{OH})_3$ colloiddally suspended in the electrolyte (and ready to dissociate as required) which is the source of the OH^- ion buffer action.

In case there is no humidity present, and because CO_2 dissolves to a considerable extent in the hot electrolyte (~ 350 cc (STP)/ $l.$ atm of 650°C carbonate melt) while it is also the only free acid species available, even a slight variation in $p\text{CO}_2$ will mean a large change in acidity since O^- solubility is orders of magnitude smaller than the CO_2 solubility. Therefore, the initial presence of any humidity to supply the H_2O (l) and OH^- species in solution even at rather low concentrations will have a strong impact on the acidity of the molten carbonate system. However, because of the very low solubility of H_2O (l), very little further quantities of weak-base will form in solution as a result of higher humidity in the gas stream. Hence $p\text{H}_2\text{O}$ will have no further influence on the acid/base character (or the Ni-solubility response) of a carbonate melt.

In Table 2 it is further shown that if this buffering behavior is a reasonably accurate representation in the molten carbonate solvent system, then there is an additional interpretation that can be given to the action of strongly dissociating alkaline additives on Ni-solubility. Considering Ni^{++} as the cation of a very weakly dissociated cathode base species such as $\text{Ni}(\text{OH})_2$ or $\text{NiO}\cdot\text{H}_2\text{O}$, it means that if a large excess reservoir of another, strongly dissociating although sparingly soluble, base species can be provided in the cathode [e.g. $\text{Mg}(\text{OH})_2(\text{s})$ or possibly $\text{Be}(\text{OH})_2(\text{s})$], this could serve to both alkalize and buffer the electrolyte against high acidity conditions in case of an excessively high $p\text{CO}_2$ pressure which unfortunately does occur occasionally and seriously damages cell performance.

Table 2
BUFFER ACTION IN PRESENCE OF WATER AND STRONG BASIC ADDITIVES
 (Effect on a Dissolved, Weak Base/Strong Acid Salt)



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TASK 5 EXPERIMENTAL DETERMINATION OF OPTIMUM ELECTROLYTE

5.1 CORROSION

Corrosion experiments and complete post-test evaluation of all coupons according to the program requirements after 500 and 3000 hour testing has been finished. It was found that the corrosion of 310S is not significantly affected by melt composition which dispells the long-standing caveat against the use of any sodium-containing melts. In order to further confirm the above finding which is so different from the earlier positions being held, two more corrosion tests in Li/K and Li/Na melts were started. The purpose of these tests is to study the corrosion of 310S over a quite long time duration (>5000 hours). The post-test coupons will be evaluated just before terminating this program.

5.2 NiO DISSOLUTION

During this reporting period, a NiO-dissolution experiment in 72Li/28K melt was carried out. The solubility is found to be 10 ± 2 wppm Ni, which is close to the result previously obtained in test series #1. The NiO-dissolution experiments and complete analyses are therefore also finished according to the program requirements.

To establish if any significant changes in melt composition occurred during the dissolution experiments as a result of electrolyte evaporation or creepage, a selected number of post-test melt samples were also sent to Northeastern University for extensive Atomic Emission Analysis of Li, Na, K, Mg, and Ba. The results indicate that there is very little change in melt composition during these dissolution experiments lasting ~200 hours.

5.3 POROUS CATHODE PERFORMANCE

AC-impedance spectra of the cathodic reaction with a 62Li/38K electrolyte have been reported recently. The spectra consist of high-frequency and low-frequency loops, which may be characterized respectively as the kinetic and mass-transfer loops. The low-frequency loop could not be observed in a 33O₂/67CO₂ atmosphere, due to very low mass-transfer resistance when this noble gas is used. This is further confirmation that oxidant activity at the 3-phase interface, which is strongly related to the gas percolation properties of a porous electrode, is an important parameter and in the present cell configuration behaves as normally observed in fuel cells. Additional experiments in 62Li/38K, 62Li/38K+Mg and 60Li/40Na melts were also performed. Figures 1 to 4 show these AC-impedance spectra at 650°C. It is clear that the use of a Li/Na melt does not cause any increases in cathode impedance, although our literature survey has indicated that some workers feel that the cathodic i_0 might be smaller in Li/Na than in Li/K melt. The ohmic resistance in the electrolyte matrix and current collectors of the test cell can be determined by extrapolating the high frequency loop of the AC-impedance curves to the real axis (see Figure 4). Metal resistance is, of course, expected to be negligible compared to electrolyte resistance, and so is ohmic resistance due to any corrosion scale in these relatively short-term duration experiments (<50 hrs.). The results of extrapolation therefore show that the resistance fraction due to the electrolyte in the matrix is lower in 60Li/40Na than in 62Li/38K melt, which confirms the electrolyte conductivities that have been reported in the literature.

MgCO₃ addition does not appear to affect the overall cathode performance significantly, although the ohmic resistance is somewhat higher than that in the non-additive Li/K melt, which could also be due to a worse contact situation between the test components. In conclusion, using a

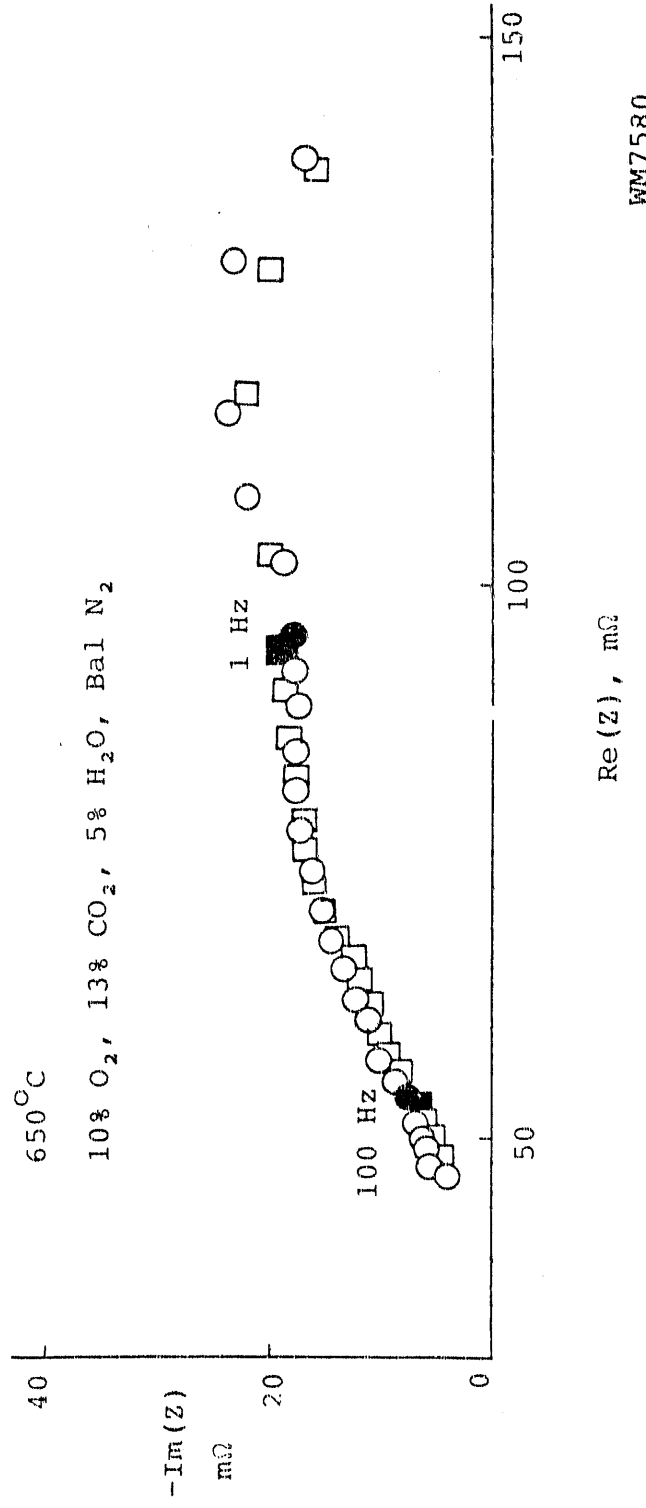


FIGURE 1 COMPLEX AC-IMPEDANCE RESULTS OF NiO CATHODE IN 62Li/38K ELECTROLYTE (DUPLICATE TESTS)

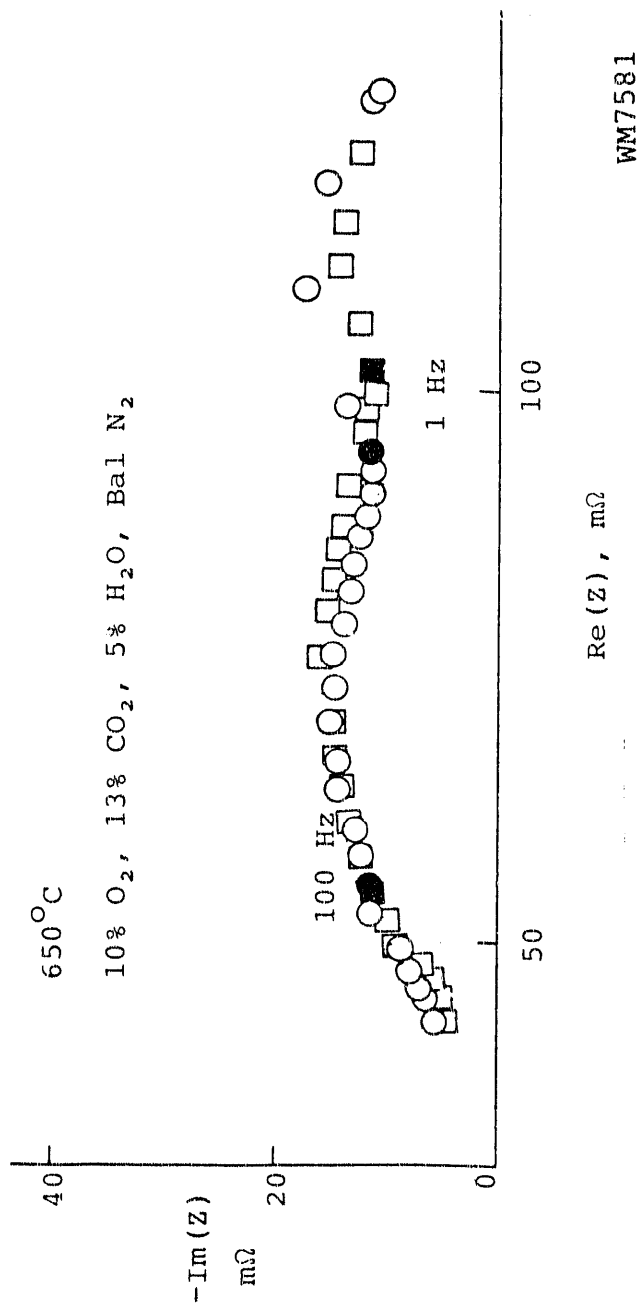


FIGURE 2 COMPLEX AC-IMPEDANCE RESULTS OF NiO CATHODE IN 60Li/40Na ELECTROLYTE (DUPLICATE TESTS)

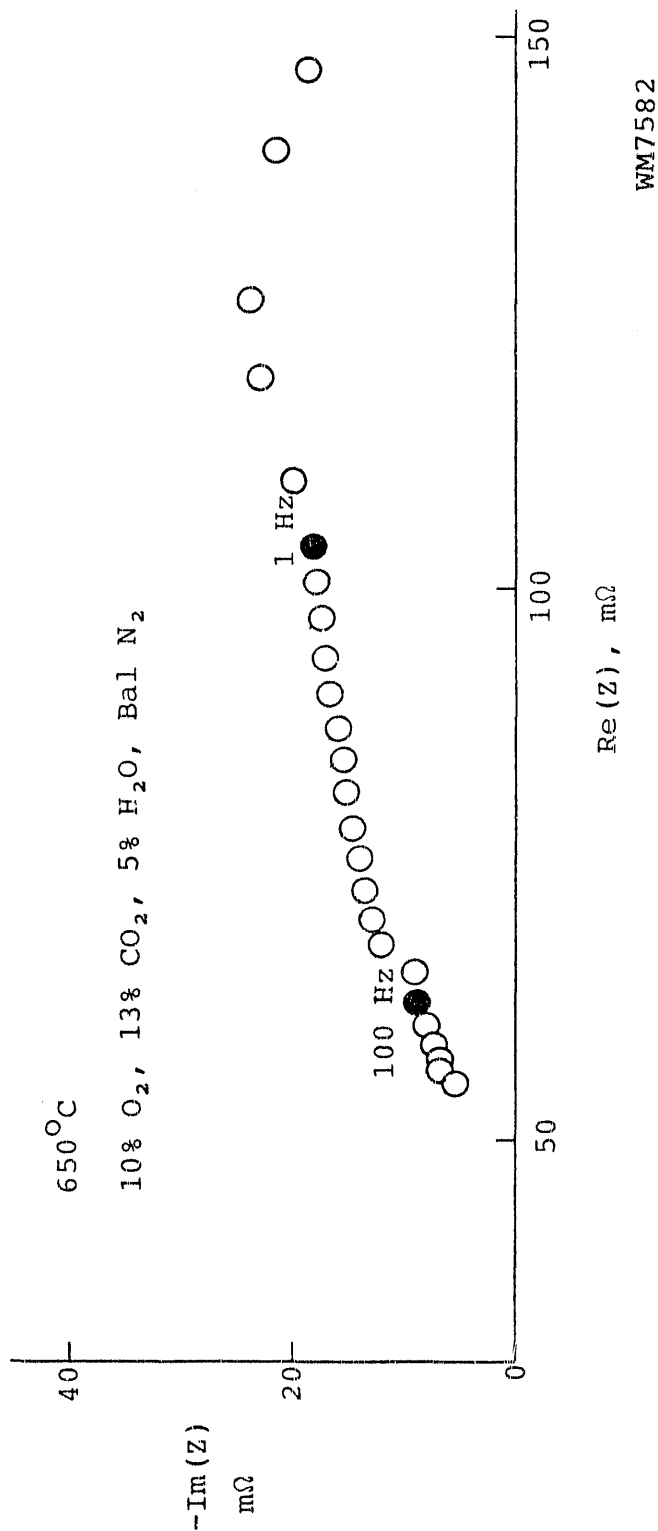


FIGURE 3 COMPLEX AC-IMPEDANCE RESULTS OF NiO CATHODE
IN 62Li/38K+Mg ELECTROLYTE

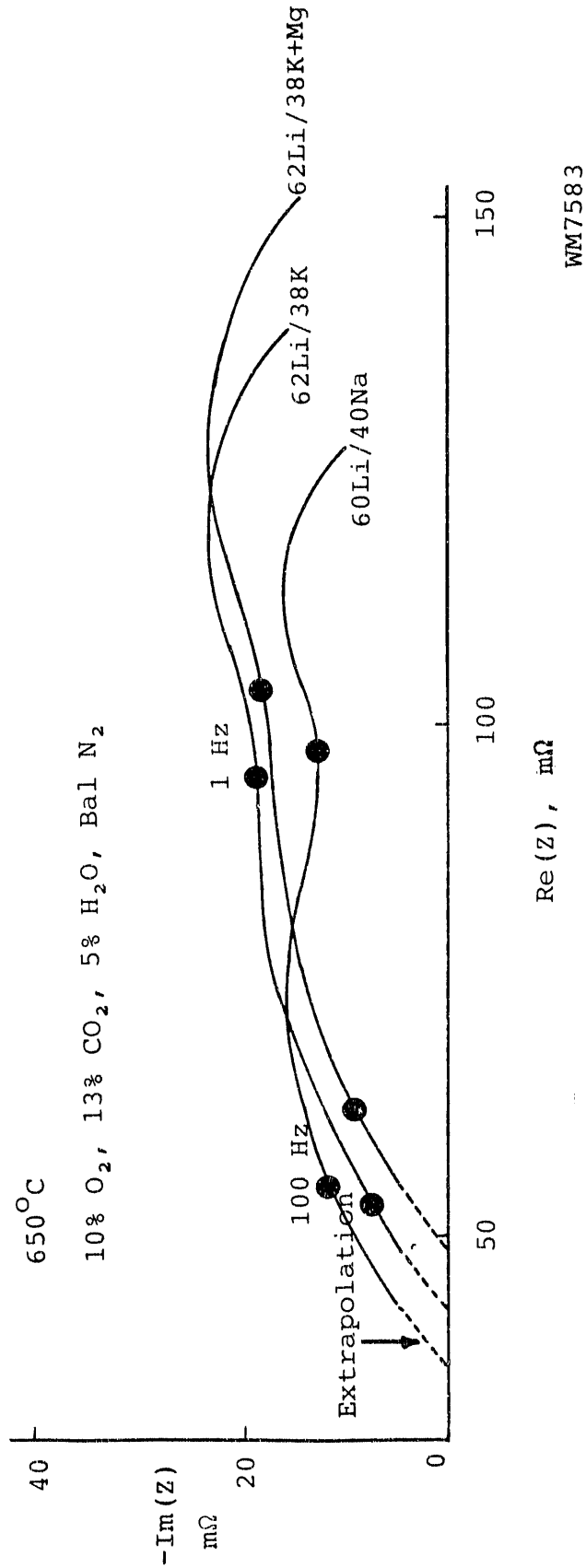


FIGURE 4 COMPLEX AC-IMPEDANCE COMPARISON OF THREE ELECTROLYTE COMPOSITIONS

Li/Na melt, although it does not appear to improve cathode kinetics a great deal, is able to reduce the overall cathode impedance. Therefore, the Li/Na melt also from this point of view appears to be a good candidate for cell testing.

5.4 LiAlO₂ STABILITY

Two duplicate sets of LiAlO₂-stability tests both in oxidant and fuel atmospheres were terminated during this reporting period after they accumulated 3000 hours. The post-test tapes were stored in a desiccator and are being sent to Foote Minerals Co. for post-test analyses. So far sixteen post-test samples of 500 hour and 3000 hour test duration in fuel and in oxidant atmosphere have now been obtained. Also three samples (i.e. the original γ -LiAlO₂ powder; a 0-hour burned out sample; and 0-hour burned out sample with carbonate impregnation) have been sent to Foote Minerals Co. for post-test analyses.

During this reporting period, a new LiAlO₂-stability experiment, in the presence of Li/K+Mg melt in anode atmosphere was also started. This test and a test started earlier in the presence of the same electrolyte but in cathode atmosphere, have both accumulated 500 hours. Both tests were cooled to room temperature and two sets of LiAlO₂ tape matrices were removed and stored in a desiccator for future analysis. The tests have been reheated to 700°C and will be terminated once they have accumulated 3000 hours.

5.6 IN-CELL TESTING

Four single cells (EM-1 through EM-4), two with 62Li/38K and two with 60Li/40Na electrolyte were started this quarter. The start-up procedure for binder burn-out and electrolyte impregnation was very similar to that used in most of ERC's testing. However, these cells showed low OCV's and G.C. diagnostics indicated relatively high cross-over. This

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cross-over and also the high resistance of these cells were probably caused by the use of a different cathode current collector structure made of 310-S alloy. This alloy was selected for the corrosion evaluation to be comparable with our out-of-cell studies but this is not absolutely essential. Follow up tests are now being readied with Type 316L current collectors having well tested mechanical characteristics.

Despite these difficulties, preliminary results from the cells with Li/Na electrolyte suggest that IR-free cell performance was on the average 40 mV better than with the standard Li/K electrolyte. Thus the first in-cell experimental indication is that the Li/Na electrolyte appears promising.

REFERENCES (continued)

- (72) Hsu, H.S., Devan, J.H. and Howell, M., "Equilibrium Solubilities of LiFeO_2 and $(\text{Li,K})_2\text{CrO}_4$ in Molten Alkali Carbonates at 650°C ," Technical Report to U.S. Department of Energy under Contract DE-AC05-84OR21400, Oak Ridge National Laboratory (August, 1986).
- (73) Lee, K.N., and Shores, D.A., "Hot Corrosion of Ni and Ni-Cr Alloys in Molten Carbonate Mixtures," Proc. Symp. High Temperature Materials Chemistry-III, The Electrochemical Society, Inc., Vol 86-2, Pennington, NJ (1986).
- (74) Lee, K.N., "Hot Corrosion of Ni and Ni-Cr Alloys in Molten Carbonate Mixtures," Ph.D. Thesis, University of Minnesota, Minneapolis, MN (1987).
- (75) Doyon, J.D., Gilbert, T., Davies, G. and Paetsch, L., "NiO Solubility in Mixed Alkali/Alkaline Earth Carbonates," J. Electrochem. Soc., 134 (12), 3035 (1987).
- (76) Broers, G.H.J., "Overview of Fundamental Research in Molten Carbonate Fuel Cells," Internal Report No. 69-0667/1272-7211, Organization for Applied Scientific Research (TNO), Apeldoorn, Netherlands (1969). (Dutch Text).

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