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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
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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.

EXECUTIVE SUMMARY

A comprehensive analysis of key properties of various carbonate blends, as well as our out-of-cell experimental work has pointed to a $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3$ blend as an attractive electrolyte mixture for the Molten Carbonate Fuel Cell. Cell life as well as performance can be enhanced significantly if this blend is used instead of the presently used $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ mixture. The next phase in ERC's effort on electrolyte optimization is to build and operate bench-scale cells with this improved composition.

Five cells have been built to date with the new electrolyte, but with moderate success: initial results show that cell performance is similar to the standard electrolyte, but some difficulties are regularly encountered with proper filling of electrodes and matrix with this blend. The problem apparently stems from poor wetting of the anode by this mixture. A reevaluation and in-depth literature probe have revealed additional data on contact angles, suggesting that $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3$ blends can indeed be less wetting as compared with $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ mixtures. These data have been discussed along with a theoretical explanation based on reported surface energies for different blends.

Remedies for this poor wetting property are proposed and will be implemented next quarter. It should be noted, however, that on the whole, less surface wetting and consequently less creepage resulting in decreases in electrolyte loss, are very desirable qualities of the Li/Na type carbonates. This is a major advantage as long as good initial electrolyte distribution and contact throughout the active components can be established and maintained.

PROGRESS BY TASK**TASK 2 LITERATURE SURVEY**

During this quarter, concerns regarding the electrolyte filling of fuel cell electrodes and matrices operating with the optimized Na-containing carbonate melt have led to a further search of the molten salt literature for up-to-date information regarding surface tension properties and wetting contact angles. Surface tension data ($\gamma_{l,g}$) based on the combined information from several sources in the U.S.(76), Australia(77), and the USSR(78) were analyzed and reported in the late 1970's in several reviews of molten carbonate properties(1,4). But these data only showed a good correlation of the surface tension properties of the alkali carbonate system in Air/CO₂ environment, as is summarized in the overall isotension diagram of Figure 1, which is derived from Hillen's work(77). This figure illustrates a 650°C version of his data which was calculated by assuming an average linear temperature coefficient. Unfortunately, no direct experimental data of wetting angles (θ) as a function of carbonate composition with respect to some solid metallic or useful ceramic surface (at acceptably high temperature and in various gas environments) were initially available.

In the early eighties, however, a further set of carbonate melt surface properties has become available which has now been carefully studied. Rasmussen of the Montana Energy R&D Institute (MERDI) performed a contact angle study in 1982 for Argonne National Laboratory(79) which addressed the effects due to trace contaminants in the carbonate melt over a range of temperatures between 400° and 750°C. Unfortunately, this work did not emphasize the use of different alkali carbonate compositions, although

**FIGURE 1 SURFACE ISOTENSIONS (mN/m) FOR THE TERNARY SYSTEM
Li/Na/K CARBONATE, ESTIMATED FOR 650°C**

a few valid runs with different composition eutectics in a reducing atmosphere were presented. This study employed one of the most difficult, although from our point of view most valuable, measurement techniques. Namely, the photographic technique of "sessile drop" contact angle measurement of a melt on polished (bright annealed) nickel surface in a reducing gas environment. This technique, in contrast to the simpler direct (i.e. ring balance) method for determining liquid/gas interfacial tensions, is of considerable value because it provides actual wetting angles with respect to a solid surface, which is a very important third parameter for our studies. However, if only gas interfacial tensions of the liquid itself are desired, then this method is at a disadvantage because the data are always obtained with reference to a some solid surface which may vary between test runs in terms of roughness and/or the presence of molecular surface films or oxide layers.

The wetting angles in the MERDI study were obtained directly from observed geometric evidence in a ($61\text{H}_2/20\text{CO}_2/19\text{H}_2\text{O}$) reducing gas environment, and therefore provide us with direct wetting information with respect to a polished, presumably non-oxidized, Ni surface relevant to the anode atmosphere. Other surfaces (e.g. solid LiAlO_2 , preoxidized Ni, Stainless Steel, etc.), and also measurements in cathode atmosphere (e.g. 40% CO_2 added to dry air) were also done, but in all these cases immediate wetting of the substrate took place which obviated any attempts at contact angle measurements. In conclusion, as shown in Table 1, there are two important aspects to be noted between the MERDI and the earlier surface tension data as they have now been reviewed. First, rather higher wetting angles generally appear to occur in reducing environment when compared to the computed values from the original data in oxidant environment. Second, a very much higher angle in contrast to the two potassium blends is shown for the

sodium melt in reducing atmosphere; i.e., $\theta > 90^\circ$ implies non-wetting at a temperature as high as 600°C . Hence, the concern with establishing a continuous electrolyte film to bridge the various cell components by capillary driving force, occurs mainly on the anode side where it could present special difficulties in connection with the Li/Na binary melt.

TABLE 1

COMPARISON OF CONTACT ANGLES, θ , FOR 3 REPRESENTATIVE MELTS IN REDUCING AND OXIDANT ENVIRONMENTS

CARBONATE COMPOSITION	FUEL*		Oxidant†
	@ 600°C	@ 650°C	@ 650°C
62Li/38K	67°	55°	$<10^\circ$ (est.)
44Li/31Na/25K	66° @ 500°C	N.A.	18°
52Li/48Na	141°	77°	32°

* Measured directly on polished, bright annealed nickel.

† Calculated from surface tension data relative to a 62Li/38K estimated wetting angle of $\theta < 10^\circ$, and by assuming the difference ($\gamma_{s,g} - \gamma_{s,e}$) in Young's equation to be independent of electrolyte composition(80).

TASK 3 ELECTROLYTE COMPOSITION SCREENING

As mentioned in previous reports, the Li/Na blend (Code N_L) in many instances has been found to be superior when compared to the various potassium-containing mixtures (e.g. S , S_L , S_X , S_M). To summarize this, the various general characteristics of sodium blends with respect to important in-cell behavior are reviewed in Table 2 by comparison to the baseline Li/K blend (S). Only when comparing these characteristics in connection with the high surface tension property (c.f. Task 2), may certain sodium-containing blends appear to possess a fairly serious

TABLE 2

SCREENING FACTORS COMPARING Li/Na WITH A STANDARD Li/K BLEND

[(+) indicates superior, (-) inferior rating]

	<u>N_L-Blend</u>
Low Melting Point	-
High Conductivity	+
Cathode, low NiO-dissolution loss	+
Cathode, low porous structure impedance	+ to =
Low Corrosion	=
Low Vaporization (calculated)	+
Desirable Surface Tension,	
- low, for electrolyte filling	-
- high, for minimal creepage	+

negative factor; namely, too high a contact angle may prevent the efficient capillary distribution of electrolyte in the active components. However, a high contact angle also implies less creepage tendency and therefore ^{less} loss of electrolyte to undersirable sites, which can be a very important endurance factor. To a major extent, the higher surface tension characteristic may therefore be a very desirable property because potassium containing blends (K_2CO_3 >25 mol%) are almost always too low in this respect, which results in excessive creepage and electrolyte rapidly moving to non-essential areas leaving active components of the cell in too dry a state. However, an excessively high surface tension and high wetting angles with little or no creepage at all may lead to the problems with electrolyte filling which have been noted. This will be further discussed under Task 5, Experimental Determinations. It is concluded that a balance must be achieved at some point to provide the optimum compromise between electrolyte retention and electrolyte transfer, which the present work is in the process of determining.

Task 5 EXPERIMENTAL DETERMINATIONS

As discussed in our last report, 3 pairs of twin bench-scale cells were recently assembled to positively determine the performance differences between the optimized sodium-containing carbonate composition (60Li/40Na, Code N_L) and conventional standard electrolyte (62Li/38K, Code S). However, some difficulties were encountered because of inadvertent mechanical breakdowns. The problems were found to be mostly of a cell related nature but a few appeared to have been aggravated by inherent surface tension differences between the two electrolytes as discussed in Task 2.

The interrelated difficulties that occurred in the initial cell tests resulted in electrolyte maldistributions, high gas cross-over and high contact and internal resistances which when taken together caused unacceptable performance variations. Reasonable cell comparisons were therefore not possible. The objective of the initial cells of course being to provide comparison between the fundamental, performance-related properties of the two carbonate blends, without the data being clouded by secondary cell interactions. Such interactions as surface tension or wetting angle differences may be inherent between the electrolytes, but these can not affect performance directly in terms of high activation or concentration polarizations or an increase in electrolyte resistance. And obviously, fuel cell operation can always be varied by small assembly and startup modifications (and/or structural adjustments) so as to improve the wetting of the cell components with electrolyte. Therefore high or low surface tension, within reason, should not be a real obstacle to good electrochemical operability.

In this respect a great deal was learned from these initial sets of cells in terms of electrolyte distribution behavior. Moreover, the data have shown that there is a definite need to take surface wetting into account for any screening or optimization testing. This is particularly necessary for the whole range of practical manipulations involved in the manufacture of a cell, its assembly and the cell start-up procedures which specifically include:

- electrolyte filling of the electrodes before assembly,
- heating and matrix burnout, as well as various gas atmosphere changes when bringing a cell up to temperature,
- final stabilization procedures when the desired fuel and oxidant gases are fed to the cell when it is put on load,
- possible thermal cycling in the event of upsets, etc.

Especially the timing, temperature and gas composition just before reaching 650°C are likely to be very important, since at 600°C it is still possible (cf. Table 1) for a Li/Na melt in anode atmosphere to remain in a completely non-wetting state (contact angle $\theta > 90^{\circ}$). Fuel and oxidant gas, when they mix at that high temperature as a result of insufficient filling of the matrix, can rapidly oxidize (i.e. burn) and lead to serious hot spots which will quickly degrade the matrix pore structure, causing a permanent cross-leak to develop. Much of our recent work, as will be shown below, has been to focus on these concerns of good initial electrolyte filling of the tape matrix after burnout.

Thus, three more cells have recently been operated. The first one with standard electrolyte (Cell 7-166 or EC-1) has now been terminated at 1000 hours and two more cells with sodium electrolyte (Cells 7-174 and 7-175) are still operating. The performance of the standard electrolyte Cell (EC-1) as illustrated in Figure 1, shows excellent cell voltage with low resistance and crossover for a period of more

FIGURE 1 LIFE GRAPH FOR CELL 7-166 (EC-1), 62Li/38K

than 500 hours, but then the cell received an upset after changing feed gas which after 150 hours caused a steady increase in contact resistance to develop. This is still being investigated but appears to have been an accidental thermal/mechanical failure.

The next two cells (EC-5b and EC-5c), as illustrated in Figures 2 and 3, are the first bench-scale sized cells to show reasonable performance with sodium electrolyte. These cells are now operating with the eutectic mixture, 52Li/48Na, instead of the previously used 60Li/40Na composition of the three earlier sodium cells. The somewhat lower concentration of lithium in the melt provides a slightly lower surface tension and eliminates any concern with cation segregation. Therefore, the cell was expected to show improved wetting without problems of electrolyte distribution. Apparently in Cell EC-5b, which was high in gas cross-over at first, this leak did improve from 10% to an almost acceptable 4%, which also slightly improved the cell voltage. But this improvement occurred only very slowly over an 800 hour period and cell resistance still showed an increase.

Cell EC-5c with slightly lighter cell hardware has shown an improvement in overall cell voltage. The cross-over is high, but may still be improving. A change in burnout procedure was made between these two cells to assist in more rapid electrolyte distribution but this may not have been sufficient. Further work on start-up conditions and slight changes in assembly and possibly a surface tension lowering electrolyte addition are contemplated for the next quarter. It is expected that a superior, non-decaying cell performance for the MCFC can be provided after a few more minor adjustments to the electrolyte and cell operating variables. Long-term tests will then be started to obtain the definitive comparison with the present standard carbonate composition.

FIGURE 2 LIFE GRAPH FOR CELL 7-174 (EC-5B), 52Li/48Na

FIGURE 3 LIFE GRAPH FOR CELL 7-175 (EC-5C), 52Li/48Na

REFERENCES

As this study progresses, repeated reference will be made to many of the same literature sources as they are surveyed for relevant information. For simplicity's sake, sections of this list will therefore be carried forward in each report where relevant and further additions will be made to it without change in the numerical sequence.

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