

ELECTROLYTE INTERACTIONS IN MOLTEN CARBONATE FUEL CELLS

Isaac Trachtenberg and David F. Cole

Texas Instruments Incorporated, Dallas, Texas

Performance data have been presented for a variety of fuel cells employing mixtures of molten alkali carbonates as electrolyte (1-6). Depending on the particular cell design chosen, the operating conditions, age of cell and a number of other parameters, almost any kind of operating characteristics (current-voltage relationships) desired can be obtained. Various investigators have emphasized certain operating characteristics; in fact, the entire experiment, cell design and operating conditions are optimized to maximize one of several parameters. Emphasis has been, for the most part, on power output per unit area of electrode and operating life. Efficiency, power output per unit weight and volume, and other fuel cell and system characteristics have received only moderate attention. However, at the present state of development it is obvious that the particular set of fuel cell system characteristics chosen will be very greatly influenced by the application. Rather than adding more fuel to the fire, this communication will emphasize certain interactions of the electrolyte which to some extent will be applicable to all molten carbonate fuel cell systems, regardless of their design and application.

There are many electrolyte interactions in a fuel cell containing molten alkali carbonates. The following text will discuss some aspects of three of these interactions: electrolyte stability in some of the gas atmospheres encountered in operating fuel cells, corrosion of silver electrodes as a function of atmosphere and electrolyte composition, and the effect of atmospheres and electrolyte composition on cathode polarization.

Electrolyte Stability

A material suitable for use as an electrolyte in a fuel cell should be chemically stable to the electrodes and atmospheric environments it will encounter during the operating life of the cell. In fuel cells employing molten alkali carbonate electrolytes CO_2 is added to the various gas streams to insure this stability. However, if insufficient CO_2 (7) is added, it is possible under certain operating conditions to obtain a condition at the cathode-electrolyte interface in which no CO_2 is present. The effects of various gas atmospheres on the stability of molten LiNaCO_3 were investigated.

Samples of 50-50 mole % Li_2CO_3 - Na_2CO_3 were exposed to various gas atmospheres at 650°C for extended time intervals, and the composition was determined by standard analytical techniques. In an atmosphere of 20% CO_2 - 80% air, tests ranging from 246 hours to 1615 hours duration indicated no decomposition of LiNaCO_3 or change in Li/Na ratio. Similar tests in 50% H_2 - 50% CO_2 for 408 hours and in 8% H_2O - 12% CO_2 - 10% O_2 - 70% N_2 for 384 hours produced no change in electrolyte composition. However, when CO_2 was not added to the air, some decomposition in the electrolyte could be detected. Data in Table I illustrate the effect of no CO_2 added to the air. The decomposition is indicated by the rise in OH^- content. Because of the analytical techniques employed both O^{2-} and OH^- present in the melt will be reported only as OH^- . There is no significant change in the Li/Na ratio. The OH^- concentration appears to remain constant after 48 hours, which indicates an equilibrium hydroxide (oxide) concentration has been established. The 0.03% CO_2 present in air may have been sufficient to prevent further decomposition.

Data for a second gas composition are also presented in Table I. The gas composition of 10% H_2O , 10% O_2 and 80% N_2 was obtained by burning a mixture of 9.5% H_2 in 76% air and 14.5% N_2 . Although there is no significant change in Li/Na ratio, there is significant decomposition of the electrolyte, as illustrated by both the decrease in % CO_3^- and the increase in % OH^- . The CO_2 content is slightly more than 3/4 of what it was in the previous experiment and can account for only a small part of the difference observed for the two gas compositions. Water removes O^- in the form of OH^- and promotes further decomposition of the carbonates. Here again, the equilibrium condition appears to be established after 21 hours, and further exposure to this gas composition produces no additional decomposition.

As pointed out by Stepanov and Trunov (7), a low ratio of CO_2/O_2 (<2.35), particularly in a cathode gas mixture containing a large amount of inert gas, results in depletion of CO_2 at the electrode-electrolyte interface and a change in electrode mechanism. This effect is further complicated by decomposition of the electrolyte, particularly if appreciable amounts of H_2O are present.

Evaporation of $LiNaCO_3$ was investigated using a radiochemical technique with C^{14} labeled $LiNaCO_3$. A sample containing C^{14} labeled $LiNaCO_3$ was placed in an Al_2O_3 boat in a tube furnace and heated to $700^\circ C$ with a mixture of 23% CO_2 - 77% O_2 flowing over the free electrolyte. The experiment was started at the time the $CO_2 - O_2$ mixture was replaced by pure N_2 . The effluent gas from the furnace was passed through a bubbler containing $Ba(OH)_2$. The $BaCO_3$ precipitate was then beta-counted at infinite thickness. The results of this experiment are shown in Figure 1. Apparently, two processes result in $C^{14}O_2$ in gas phase. The first process appears to fall off rapidly (an order of magnitude change in one hour) and is essentially complete in about six hours. The second process, which is much slower, shows only a slight decrease with time up to 250 hours. The first process (fast) is believed to be the decomposition of $LiNaCO_3$ into $LiNaO$ and CO_2 . The second process (slow) is believed to be the evaporation of $LiNaCO_3$. This slow process has an approximate rate of 10^{-5} mole of CO_2 per mole of N_2 passed. Broers (1) reported that in an operating fuel cell containing Li, Na and K carbonates evaporation losses were about 10^{-5} mole of CO_3^- per mole of fuel, air and CO_2 passed over the electrolyte.

Evaporation losses were also determined by very careful weight loss measurement. A sample of 30% $LiNaCO_3$ - 70% fused MgO was mixed in an Al_2O_3 boat and placed in a tube furnace at $700^\circ C$. A gas mixture of 5% O_2 , 12% CO_2 , 83% N_2 was passed over the electrolyte mixture. Three separate runs of 123, 113 and 117 hours were made. The total gas flow was 3.2 moles/hr for the first two runs and 3.5 moles/hr for the third run. The average weight loss for the three runs was 6×10^{-5} gram/mole of effluent $\pm 3 \times 10^{-5}$ gram/mole of effluent. Two runs of 117 and 161 hours were made using pure N_2 at 2.0 and 2.1 moles/hr. The average weight loss was 4.9×10^{-4} gram/mole of effluent $\pm 0.9 \times 10^{-4}$ gram/mole of effluent. The sample was then re-exposed to the first gas mixture containing CO_2 for 17 hours. The weight of the sample increased by an amount that was 68% of the weight lost during the N_2 runs. This is equivalent to 7.5×10^{-6} mole of CO_2 /mole of gas effluent, assuming that this portion of the weight loss can be attributed to electrolyte decomposition. The net evaporation loss during the N_2 runs is 1.6×10^{-4} gram/mole of gas effluent. If the latter weight loss is assumed to be $LiNaCO_3$, this represents an additional CO_2 loss of 2×10^{-6} mole/mole of effluent gas. The total loss of CO_2 during the N_2 runs thus became 0.95×10^{-5} mole/mole of N_2 , which agrees very well with the 1×10^{-5} mole/mole of N_2 found by the radiochemical technique.

The rate of evaporation loss appears to be higher in the absence of CO_2 in the gas phase (1.6×10^{-4} vs 0.6×10^{-4} gram/mole of N_2). However, both values have considerable uncertainty, and the difference may not be significant.

These studies indicate that electrolyte stability (decomposition and/or evaporation) may well become a problem in long-lived molten carbonate fuel cells. Further, they point up the requirement for sufficient CO_2 in contact with the electrolyte, particularly in the cathode gas where relatively large amounts of inerts will be present if air is used as the O_2 source. The suggestion of Stepanov and Trunov (7) that the CO_2/O_2 ratio be about 2.35 should be seriously considered by molten carbonate fuel cell system designers.

Silver Corrosion

The corrosion of silver in molten carbonates has been studied by several groups (10, 11, 12) and observed qualitatively by many others, but the conditions employed in the experiments have not been representative of the operation of a molten carbonate fuel cell except for those reported by Broers (8).

The results presented here were obtained by weight loss measurements. The samples used were 20 gauge silver wire, 5.1 sq cm in geometric surface area. The samples were immersed completely and to a uniform depth in either 50% Li_2CO_3 - 50% Na_2CO_3 or 37% Li_2CO_3 - 39% Na_2CO_3 - 24% K_2CO_3 contained in an 80% Au - 20% Pd crucible of 250 cc capacity. Atmospheric composition was maintained at 90% N_2 - 10% CO_2 until the desired operating temperature was reached and thereafter was maintained at the desired composition as determined by Orsat analyses. The most extensive experiments have been performed in an atmosphere (5% O_2 - 10% CO_2 - 85% N_2) believed likely to be typical of operating conditions in molten carbonate fuel cell systems using air and spent fuel in the cathode gas supply. (In operating fuel cell systems about 10% of N_2 will be replaced by H_2O .)

Visual examination of the weight loss samples after completion of the experiments indicated apparently uniform attack with no dendritic growths from reprecipitation of dissolved silver.

Table II lists the results of experiments under a variety of atmospheric conditions in binary melts. Weight loss was negligible in the pure CO_2 atmosphere at 600°C. Where oxygen was present, the rate of weight loss increased with increasing partial pressure of oxygen.

Table III shows the constancy with time of the weight loss of the silver samples in both ternary and binary carbonate melts under the conditions shown.

There is no significant difference in rates in the binary and ternary mixtures. Accordingly, the rate-limiting process is apparently not the diffusion of dissolved oxygen to the metal surface but rather a process such as diffusion of silver ions away from the dissolution sites.

Diagrams analogous to those of Pourbaix have been constructed by Ingram and Janz (13) to show the thermodynamic positions of metals in ternary molten carbonate eutectic with respect to corrosion as a function of O_2 and CO_2 partial pressures. These gases determine the O_2/O^- redox potential in the melt.

There are important factors which would tend to make the corrosion of silver in operating molten carbonate fuel cells less severe than in these experiments. These factors include cathodic polarization of the silver electrode when the cell is subjected to current loading, immobilization of the electrolyte by the matrix and the limited amount of electrolyte available in the cell.

Cathode Polarization and Melt Composition

The solubility of oxygen in molten alkali carbonate mixtures has recently been shown by Broers to be dependent on the melt composition (8).

Oxygen was found to be more soluble in ternary (Li, Na, K) than in binary (Li, Na) mixtures. This seems ample reason to suspect that polarization of the molten carbonate fuel cell cathode (an oxygen - carbon dioxide electrode) is also dependent on melt composition. This has been observed experimentally.

Presented here are the results of a series of experiments in which the IR-free polarization of silver cathodes has been determined in melts of two compositions, 50%* Li_2CO_3 - 50% Na_2CO_3 and 37% Li_2CO_3 - 39% Na_2CO_3 - 24% K_2CO_3 . Temperature was varied from 600 to 780°C. Partial pressures of CO_2 and O_2 were fixed so that CO_2/O_2 was about 2-2.5 and were determined by Orsat analysis. These experiments were performed in operating fuel cells of a design which has been previously described (2). The silver cathodes were 1 in. x 4 in. and were constructed of 120 mesh twill weave screen with 3.7 mil wire diameter. The resistance measurements for the IR corrections to the polarization were made by a current interruption technique which has also been described previously (8). Voltages were measured with respect to either a Danner-Key Ag/Ag^+ reference electrode or a Ag-wire idling oxygen electrode. Reproducibility of voltages was quite satisfactory in both cases.

Figures 2 and 3 show the effects of temperature on the cathode polarization in binary and ternary electrolyte, respectively, at a fixed gas composition of 15% O_2 and 30% CO_2 (55% N_2). Figure 4 combines some of the data of Figures 2 and 3 for easier comparison. Figure 5 presents data exhibiting the effect of gas composition on cathode polarization in the two carbonate mixtures at a fixed temperature (700°C). It should be noted that the data at higher oxygen concentration (in the gas phase) were more reproducible, partly because of the greater ease of measuring and maintaining constant the gas composition.

What is the cause of this electrolyte composition effect? The structure and properties of molten alkali carbonates and other ionic liquids are known to depend on the particular alkali metal ions present (14). As the size of the alkali metal ion increases, the volume expansion of the carbonate on melting increases. Most of this volume expansion is accounted for by introduction of "holes" into the melt structure. The smaller cations have a greater tendency to become involved in formation of ion-pairs, but the larger ions are more effective in stabilizing other complex ions which may be formed.

Janz (15) reported that experimentally determined conductances, surface tensions and densities are much nearer the values computed by simple additivity relationships in the case of a Li_2CO_3 - Na_2CO_3 mixture than in that of a Li_2CO_3 - Na_2CO_3 - K_2CO_3 or a Li_2CO_3 - K_2CO_3 mixture.

The heat of solution of oxygen, like the activation energies for viscosity and conductance (16), is higher for the ternary than for the binary (Li-Na) mixture. All these properties seem related to the degree of dissimilarity of the cations. Most attempts (17) at explanation of this behavior have been in terms of competition of the cations for certain orientations with respect to the carbonate ion, the larger cations orienting so as to allow more freedom of rotation for the anion.

* mole %

Improvements in cathode polarization in molten carbonate fuel cells utilizing ternary electrolyte are not, unfortunately, directly reflected in greater power densities than those of cells using binary electrolyte. Anode polarization in the ternary electrolyte cells is poorer than that in the binary electrolyte cells, so power densities do not differ significantly. However, the electrolytic composition might be chosen so as to improve power output if there is a considerably more severe polarization of one electrode in a cell than of its counterpart.

Anode polarization behavior may be clarified by determinations of hydrogen solubility in the melts.

SUMMARY

Studies of three areas of influence of molten carbonate fuel cell system operating conditions on interactions with the electrolyte have helped to define certain problems which may arise. Electrolyte loss (decomposition and evaporation) may be minimized by optimizing CO_2 distribution to the electrolyte-gas interface. Corrosion of silver is increased by raising O_2 partial pressure in the cathode gas supply but there is little latitude for change in this composition in a system utilizing air and spent-fuel CO_2 . Cathode polarization characteristics are better in Li-Na-K ternary melt than in Li-Na binary melt but power densities are not significantly different because of anode polarization behavior.

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Table I
LiNaCO₃ Electrolyte Composition as a Function of Time at 650°C

Hours	Gas Composition 100% Air				Li/Na
	%CO ₃ ⁼	%OH ⁻	%Na ⁺	%Li ⁺	
0	66.6	0.0	25.7	7.5	.29
3	66.7	0.2	25.6	7.5	.29
48	66.9	0.5	26.4	7.6	.29
98	66.8	0.5	26.4	7.9	.30
144	67.2	0.4	26.4	8.1	.31
216	66.6	0.5	26.2	7.8	.30
336	67.1	0.6	26.0	7.9	.30

Hours	Gas Composition 10% H ₂ O - 10% O ₂ - 80% N ₂ (9.5% H ₂ - 76% Air - 14.5% N ₂)				
	%CO ₃ ⁼	%OH ⁻	%Na ⁺	%Li ⁺	Li/Na
0	66.5	0.0	25.7	8.0	.31
3	65.1	1.2	25.5	8.0	.31
21	63.5	3.1	25.6	8.3	.32
71	64.1	3.2	25.6	8.0	.31
165	64.0	2.1	25.7	8.1	.32
333	62.4	3.0	25.9	8.1	.31
477	63.3	2.3	25.9	8.2	.32

Table II
Silver Corrosion in Molten Alkali Carbonates

Electrolyte: 50 Mole % Li₂CO₃ - 50 Mole % Na₂CO₃

Area of Sample: 5.09 Sq. Cm.

Time (Hrs)	Temperature °C	Gas Composition %			Wt. Loss (Mg/Cm ²)	Rate of Wt Loss (Mg/Cm ² Hr)
		O ₂	CO ₂	N ₂		
100	600	--	100	--	<.06	<.0006
48	600	5	12	83	5.1 ± 1.1	0.11 ± 0.02
168	600	5	10	85	17.9 ± 0.2	0.11 ± 0.02
100	600	10.5	89.5	--	20.6 ± 2.8	0.20 ± 0.03
111	600	27.5	72.5	--	40.8 ± 2.2	0.36 ± 0.02

Table III

Silver Corrosion in Molten Alkali Carbonates

Electrolyte: 37 Mole % Li_2CO_3 - 39 Mole % Na_2CO_3 - 24 Mole % K_2CO_3

Area of Sample: 5.09 Sq. Cm.

Time (Hrs.)	Temperature (°C)	Gas Composition (%)			Wt. Loss (Mg/Cm ²)	Rate of Wt. Loss (Mg/Cm ² /Hr)
		O ₂	CO ₂	N ₂		
26	700	5	10	85	6.2 ± 0.8	0.24 ± 0.03
48	700	5	10	85	10	0.21
95	700	5	10	85	21.8 ± 1.2	0.23 ± 0.01

Electrolyte: 50 Mole % Li_2CO_3 - 50 Mole % Na_2CO_3

Area of Sample: 5.09 Sq. Cm.

Time (Hrs.)	Temperature (°C)	Gas Composition (%)			Wt. Loss (Mg/Cm ²)	Rate of Wt. Loss (Mg/Cm ² /Hr)
		O ₂	CO ₂	N ₂		
24	700	5	10	85	5.8 ± 0.7	0.24 ± 0.03
48	700	5	10	85	8.0 ± 1.3	0.17 ± 0.03
72	700	5	10	85	18.5 ± 1.5	0.26 ± 0.02
96	700	5	10	85	21.5	0.22

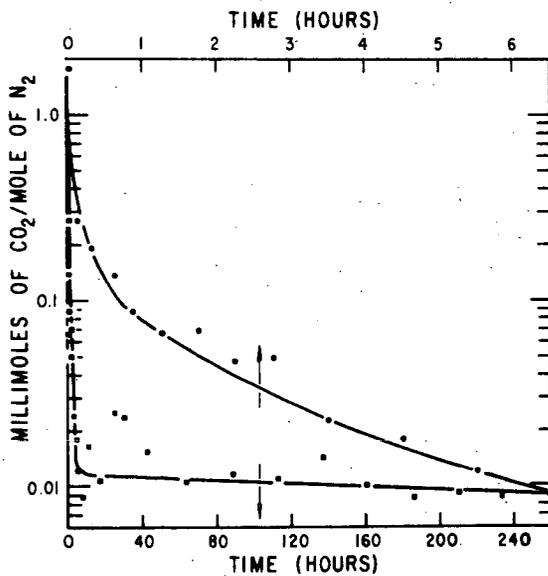


Fig. 1. Rate of CO_2 evolution from LiNaCO_3 at 650°C

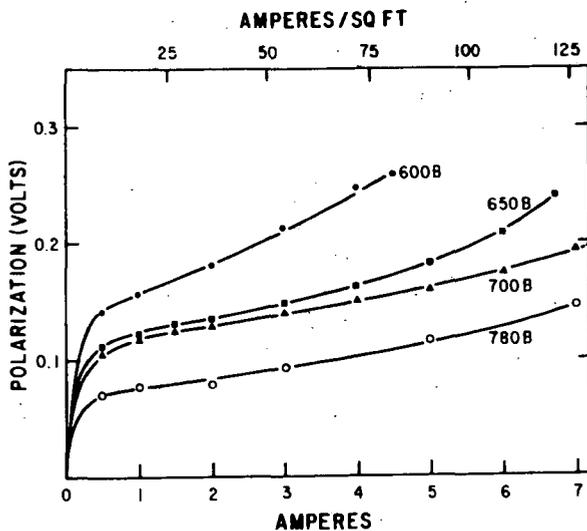


Fig. 2. Cathode polarization in binary (Li-Na) electrolyte vs temperature ($^{\circ}\text{C}$). Gas composition: 15% O_2 , 30% CO_2 , 55% N_2

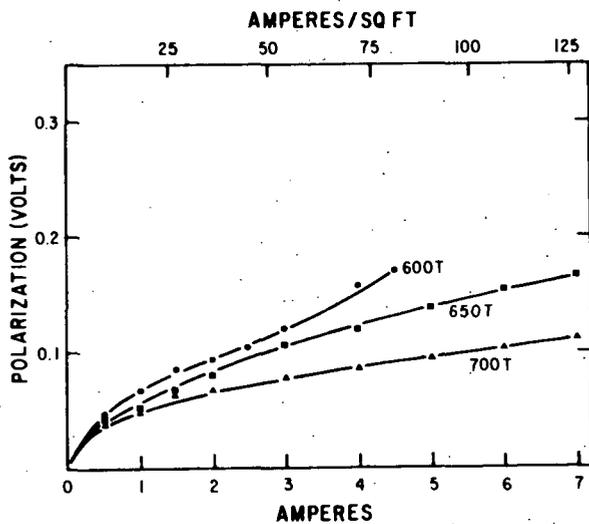


Fig. 3. Cathode polarization in ternary (Li-Na-K) electrolyte vs temperature ($^{\circ}\text{C}$). Gas composition: 15% O_2 , 30% CO_2 , 55% N_2

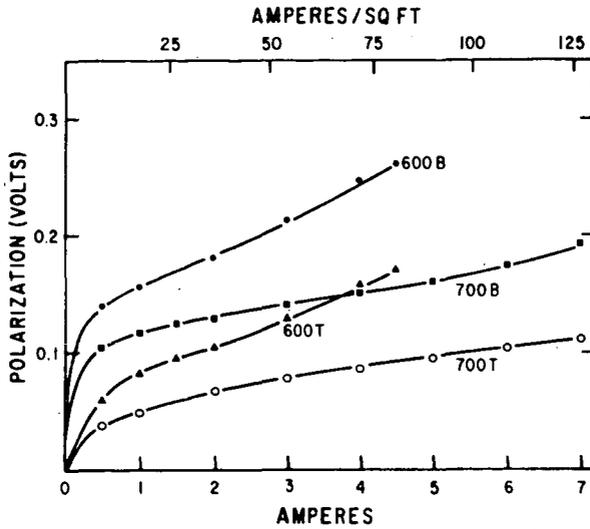


Fig. 4. Cathode polarization in binary (B) and ternary (T) electrolyte vs temperature ($^{\circ}\text{C}$). Gas composition: 15% O_2 , 30% CO_2 , 55% N_2

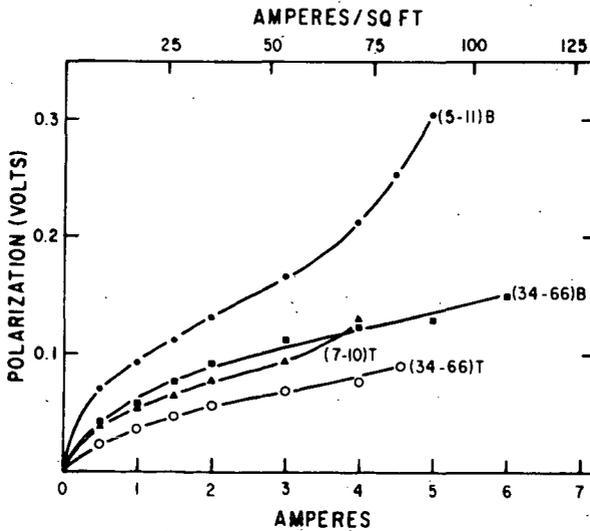


Fig. 5. Cathode polarization at 700°C in binary (B) and ternary (T) electrolyte vs gas composition (% O_2 - % CO_2).