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Abstract
Earlier electrolyte segregation tests of Li/Na carbonate used chemical analysis such as inductively coupled plasma/atomic emission spectroscopy (ICP/AES) of matrix strips wetted with carbonate and exposed to 5- to 20-V potential gradients. A segregation factor was correlated to the Li/Na carbonate composition. While fairly substantial segregation occurs at the eutectic composition of 52% Li, it is minimal at 60% to 75% Li. Such lithium-rich Li/Na carbonates may not be practical because the melting points are too high (i.e., liquidus point is 625 °C). By adding calcium and barium to the lithium/sodium carbonates, we were able to lower the melting point and maintain nonsegregating behavior. This work is directed at examining the long-term stability of the quaternary Li/Na/Ba/Ca electrolytes. Electrolyte optimization work evaluates Li/Na ratio and Ba/Ca level to improve cell performance at 320 mA/cm² and reduce temperature sensitivity. A number of cells with quaternary Li/Na/Ba/Ca electrolytes ranging from 3 to 5% Ba/Ca have operated well with stable, long-term performance. Congruent melting carbonate is important for commercial development. The best so far is 3.5% Ba/Ca/Li (3.5 mol% /3.5 mol% Ba/Ca) carbonate (m.p. 440°C). Performance at 160 mA/cm² is increased up to 150mV as compared with the baseline cell containing the Li/Na eutectic composition. Life stability has been reproduced by a number of bench-scale MCFC test with operations of 2000-4300 h and the electrolyte composition across the matrix little changed.

Background
Our earlier investigation of various Li/Na ratios of carbonate electrolyte for the molten carbonate fuel cell (MCFC) revealed an apparent correlation between improved bench-scale MCFC performance and nonsegregating electrolyte compositions [1]. Differences in the ionic mobility, as with lithium and potassium ions in Li₂CO₃/K₂CO₃, have long been known to lead to changes of the composition between the positive and negative side of the fuel cell. As a result, the melting point and other physical properties of the electrolyte can vary at different locations in the fuel cell. Electrolyte segregation has been reported to occur within both the MCFC and the stack [2]. In the cell, the segregation increases the potassium concentration near the cathode, which leads to increased cathode
solubility and consequent performance decline. In the stack, the high potential difference on the gaskets causes electrolyte migration and cation segregation, which leads to severe performance decline of the “end” cells. The trend in electrolyte fill versus composition is analogous to that of electrolyte segregation. The greatest change occurs with the eutectic Li/Na carbonate, which also displays the greatest cation segregation. We found that Li/Na carbonate electrolyte migration tends toward the cathode. This migration pattern is the opposite of what is found using Li/K carbonates. Indeed, post-test examinations of bench-scale Li/Na cell tests have shown flooded cathodes.

The objective of electrolyte development at Argonne National Laboratory is to develop molten carbonate electrolyte compositions that have minimal segregation in the individual fuel cell and cell stack under an electric field. The Li/Na carbonate electrolyte is receiving increased interest by MCFC developers as a replacement for Li/K electrolyte [3-6]. Our approach is to characterize Li/Na carbonate mixtures in terms of their segregation properties in an electric field and, if necessary, to modify the observed segregation by adding Ba and Ca carbonates. The recent literature has provided comparisons of Li/K and Li/Na carbonates for performance and life. Generally, the findings favor the Li/Na carbonate [7], but an apparent drawback is its greater temperature sensitivity [8].

Investigations of ex situ cation segregation used 12-cm-long strips, wetted with carbonate and exposed to 5- to 20-V potential gradients. These conditions simulate the gasketing strip of an externally-manifolded MCFC. The strip was purged with a 1:2 O₂:CO₂ gas mixture (500 ml/min) at 655°C. After 72 h at 20 V, the potential distribution in the strip reached equilibrium. These strips were sectioned for chemical analysis by inductively coupled plasma/atomic emission spectroscopy (ICP/AES). The variation in cation composition versus strip length was linear; therefore, these deviations were represented as a single cation separation value, or "segregation factor," given in terms of (mol%)/cm. When the ICP/AES results of electrolyte segregation were correlated to the Li/Na carbonate composition, it was found that the nonsegregating range was 65-75 mol% Li. Surprisingly, the eutectic 52/48 Li/Na carbonate displays the greatest cation segregation. Even the Na-rich side of the eutectic composition, 40/60 Li/Na carbonate, exhibits lower cation segregation than does the eutectic. An electrolyte is considered non-segregating when the two cations have equal mobilities (the Chemla Effect). With equal cation mobilities, electrolyte migration should also be minimized.

Bench-scale (100-cm²) MCFC tests using off-eutectic Li/Na electrolytes show increased performance at 160 mA/cm², compared with the baseline cell containing the eutectic 52/48 Li/Na composition. Cell tests were completed with six Li/Na electrolyte compositions: 40/60, 52/48, 60/40, 67/33, 71.5/28.5, and 75/25 (in mol%). These cell tests indicate that electrolytes in the composition range of 65-75 mol% Li improve cell performance over the 52/48 Li/Na eutectic. Increases in electrolyte lithium content from 52/48 to 71.5/28.5 Li/Na improved the cell potential by 75 mV. The study of the polarization behavior of the six MCFC cell tests was conducted with fuel and oxidant utilizations of 60% and 40%, respectively, at 320 mA/cm² and 650°C. Cell impedance, a combination of IR losses and electrode polarization, is reduced in off-eutectic compositions: 0.8 ohm cm² for 71.5/28.5 Li/Na compared to 1.4 ohm cm² for 52/48 Li/Na eutectic. Again, the eutectic 52/48 Li/Na carbonate displays the greatest cell impedance, as well as the greatest cation segregation. Only a minor portion of the reduced cell polarization can be attributed to increased electrolyte conductivity that is associated with the increased Li₂CO₃ content.
The results show a strong correlation between nonsegregating characteristics and improved cell performance. Nonetheless, these cell tests indicate that electrolytes in the composition range of 65-75 mol% Li improve cell performance over the 52/48 Li/Na eutectic that is commonly used. However, such lithium-rich Li/Na carbonates may not be practical, because the melting points are too high (i.e., liquidus point is 625 °C).

**Development of Li/Na/Ba/Ca Carbonate Electrolyte for High Performance**

Electrolyte segregation can cause the melting point and other physical properties of the electrolyte to vary at different locations in the MCFC and lead to performance decline. Argonne National Laboratory has identified nonsegregating electrolyte compositions that not only eliminate these effects, but also indicate significantly improved MCFC performance [1]. Various Li₂CO₃-Na₂CO₃ compositions have been screened for nonsegregation. It is evident that fairly substantial segregation occurs at the eutectic Li/Na carbonate composition of 52% Li₂CO₃, but between 60 and 75% Li₂CO₃, segregation is minimal. Such lithium-rich salts may not be practical, however, because the melting points are too high. By adding calcium and barium to the lithium/sodium carbonates, the melting point was lowered and non-segregating behavior maintained, Figure 1.

As a result of examining the melting characteristics of approximately two dozen carbonate compositions between 2 to 5 mol% Ba/Ca, a 3.5% Ba/Ca/Na/Li quaternary carbonate was found to completely melt into the porous Ni at 600°C. This more congruent melting Li/Na/Ba/Ca carbonate had its melting point determined by an acoustic method. The melting point is quite sharp at 465°C with the onset of melting at 440°C.

To determine the relation between electrolyte composition and electrochemical behavior in the fuel cell, we ran cell tests for various quaternary electrolytes, Li/Na compositions with Ba/Ca additions. Bench-scale (100 cm²) MCFC tests were assembled with standard Ni anodes (3% Cr) and Ni-based cathodes. Cells with Ba/Ca/Na/Li carbonate use both tape-cast electrolyte and matrix layers and use a standard binder-burnout schedule for cell startup. Cells were operated at 650°C for life testing, and over the temperature range of 575-675°C to establish performance versus temperature characteristics. Performance data of the bench-scale tests at 160 mA/cm² were used to compare the performance of 3.5% Ba/Ca/Na/Li electrolyte compositions in three types of MCFC Cell design. Data on cell impedance, cell voltage, and electrode performance at various utilizations and current-density operations were monitored as a function of time at 1 atm with laboratory standard oxidant (air + 28% CO₂) and humidified fuel (80% H₂ + CO₂).

Bench-scale MCFC tests using ternary electrolytes show increased performance at 160 mA/cm², up to a 150-mV increase, compared with the baseline cell containing the Li/Na eutectic composition (Figure 2). We identified a range of quaternary electrolyte compositions of Li/Na/Ca/Ba carbonate that generally improves MCFC operation and performance. These improvements include high current-density operation (250-360 mA/cm²), reduced temperature sensitivity, and anticipated extended life. Cells with 3.5% Ba/Ca/Na/Li electrolyte show optimum performance.
Effect of Temperature

Reduced temperature sensitivity is demonstrated of 3.5% Ba/Ca/Na/Li electrolyte compared to Li/Na carbonate (Figure 3). Like the melting point for the quaternary Ba/Ca/Na/Li electrolytes, the improved MCFC performance/temperature characteristic is maximized at 3.5% over either a 3% or a 4% Ba/Ca addition. Compared to the Li/Na eutectic composition at 600 °C, the MCFC performance is increased by about 200 mV. The MCFC test voltage is well above 0.8 V at 600°C. This level of performance is similar to the expectations for Li/K carbonate electrolyte at 600 °C. Although performance has varied for other 3.5% Ba/Ca/Na/Li electrolyte cells, the slope of cell voltage versus cell-operating temperature is similar between 575 and 675°C. Variation in the V/I curve between cells is apparently related to the cell’s resistive component. Reduced temperature sensitivity with the 3.5% Ba/Ca/Na/Li electrolyte is retained with humid oxidant gas (Figure 4).

Others have explained the effect of temperature upon MCFC performance as related to the solubility oxidant in the electrolyte and the surface tension [8]. These properties have not yet been measured for the quaternary Ba/Ca/Na/Li electrolytes. The propensity of eutectic Li/Na carbonate electrolyte to segregate and consequently transition to a higher-melting-point composition is another likely cause for its reduced performance at lower temperature. Our plans are to measure wetting angles of Li/Na carbonate and quaternary Ba/Ca/Na/Li electrolytes to gain further understanding.

Effect of Oxidant Composition

Commercial developers of MCFC rely on balance-of-plant considerations to determine oxidant composition. The oxygen partial pressure for commercial MCFC is usually less than the 30% CO₂-Air that is typically applied to laboratory tests. Our MCFC test results for different oxidant compositions also show good performance with the Ba/Ca/Na/Li electrolyte. As in Figure 5, there is little change in polarization curves for a change in oxidant composition from Reference Oxidant RO (30% CO₂-air) to Humid System Oxidant SO (8% CO₂-8% O₂-59% N₂-25%H₂O), about 30 mV at 650 °C. The reduced open-circuit-voltage, OCV, accounts for 20mV of the change. The MCFC performance with a 70% dilution of the oxidant gas (i.e., humid SO) indicates good electrode kinetics, no cathode mass-transport limitations with the quaternary 3.5% Ba/Ca/Na/Li cell. That is, the cathode structure and the level of electrolyte content (wetting) provide good mass transport, such that the reduced oxidant activity does not have pronounced effect on cell performance. Sishlta et. al. explain the effect of temperature and oxidant partial pressure on MCFC performance to related to dominance of either the super oxide or peroxide electrode mechanisms [9]. The peroxide mechanism would favor stable performance with a change in oxidant quality. On the other hand, the super oxide mechanism favors performance stability relative to temperature change. The quaternary 3.5% Ba/Ca/Na/Li electrolyte seems to combine favorable effects of both of the competing mechanisms.

Life Stability

The objective of our life testing is to demonstrate retention of improved performance with the quaternary 3.5% Ba/Ca/Na/Li electrolyte. Past bench-scale MCFC tests have been operated for life at a current density greater than 160 mA/cm², or 240 mA/cm², and exhibited stable performance. A further objective is to show stable life with humid cathode
oxidant gas, which addresses operating conditions of commercial MCFC, see Figure 6. These conditions raise concerns for increased cathode corrosion, but LiAlO₂ matrix stability, electrolyte creep, and electrolyte volatility also come into play. The specific interest of this study is electrolyte segregation. The performance of 3.5% Ba/Ca/Na/Li Cell No.10 remained stable for 4300 h with humid oxidant gas. In post-operative analysis, one-third-thickness sections of the LiAlO₂ matrix were submitted for chemical analysis. The electrolyte compositions remained within a 2 mol% deviation from the starting compositions: effectively nonsegregating. A current MCFC is showing improved performance at 650 °C of 0.90 V at 160 mA/cm², which is the result of adjusting cathode pore size [10]. For the benefit of commercial developers, the No.10 (see Figure 7) is operating at 600 °C for reduced cathode solubility and cathode current-collector corrosion.

Conclusions

The nonsegregating property of the carbonate and its composition at the electrode/electrolyte interface plays a significant role in the MCFC performance. At this point, we are not certain whether the improvement in cell potential is due to lower overpotentials, but we have ascertained the stability of the cell potentials over at least four thousand hours. Remarkably, the potentials remain stable even at current densities of 240 mA/cm². Bench-scale MCFC tests support DOE contractor adaptation and optimize the Ba/Ca/Na/Li composition for performance, reduced corrosion, and stable operating life. Transferring this technology to commercial developers will aid its adaptation. Electrolyte optimization work also indicates lower cell impedance. Duplicate-cell tests with 3.5% Ba/Ca/Na/Li carbonate also exhibit stable performance at 320 mA/cm². We find reduced temperature sensitivity for MCFC with 3.5% Ba/Ca/Na/Li, compared to both 4% and 3% Ba/Ca/Na/Li carbonate electrolytes, such that MCFC operation at 600°C may be practical.

Acknowledgments

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References


10. E. Haugh, M-C Power, personal communication

[Diagram: Figure 1 (ICP/AES) analysis for cations at positions on a matrix strip (12 cm long) wetted with carbonate and exposed to 5- to 20-V potential gradients. Ba/Ca addition mitigates cation segregation.]
Figure 2. Voltage/current tests of MCFC using ternary electrolytes compared with the baseline cell containing the Li/Na eutectic composition. Performance increased by 150 mV at 160 mA/cm².

Figure 3. Reduced temperature sensitivity of 3.5% Ba/Ca/Na/Li electrolyte compared to Li/Na (52/48 mol%) carbonate.
Reduced temperature sensitivity of 3.5% Ba/Ca/Na/Li electrolyte is maintained despite humid oxidant gas.

Polarization curves for a change in oxidant composition from Reference Oxidant (RO) (30% CO\textsubscript{2}-air) to Humid System Oxidant (SO) (8% CO\textsubscript{2}-8% O\textsubscript{2}-59% N\textsubscript{2}-25%H\textsubscript{2}O).
Figure 6. Life Plot to 4300 h for tapecast-type MCFC 3.5% Ba/Ca/Na/Li No. 9, showing voltage at 160 mA/cm².

Figure 7. Life Plot to 600 h for tapecast-type MCFC 3.5% Ba/Ca/Na/Li No. 10 showing voltage at 160 and 240 mA/cm² using dry RO gas.