NONSEGREGATING ELECTROLYTES
FOR MOLTEN CARBONATE FUEL CELLS

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INTRODUCTION

In the current technology, molten carbonate fuel cells (MCFCs) employ a lithium-potassium carbonate mixture. The mixture, usually 62 m/o Li_2CO_3 and 38 m/o K_2CO_3 (abbreviated as 62/38 Li/K), melts below about 550°C and, when mixed with lithium aluminate, serves as both the electrolyte and gasketing for the cell and cell stack. Electrolyte segregation has been reported [1] to occur within both the cell and stack. In the cell, the segregation increases the potassium concentration near the cathode and leads to increased cathode solubility and performance decline. In the stack, the high potential difference on the gaskets causes electrolyte segregation, which in turn leads to severe performance decline of the end cells.

Argonne National Laboratory is developing molten carbonate electrolyte compositions which have minimal segregation in the individual fuel cell and cell stack under an electric field. The Li/Na carbonate electrolyte is receiving increased interest [2-5] by MCFC developers as a replacement for Li/K electrolyte. 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.

Results of gasket strip (20 V) screening studies, as well as those from cell tests, will be discussed. We found that MCFC performance is linked to the nonsegregating property of the electrolyte. Cation distribution from segregation tests was generally linear and could be expressed as a segregation factor. A reduction in electrolyte segregation factor reduced cell polarization proportionally. The reduced cell polarization exceeds improvements that could be attributed to increased electrolyte conductivity.

OBJECTIVE

We are identifying nonsegregating Li/Na carbonate electrolyte compositions because others have shown [2-5] that the Li/Na electrolytes show promise in extending the operating life of MCFC. We correlated cell performance with electrolyte segregation behavior. Our further objective is to overcome problems related to electrolyte segregating and thus improve MCFC performance. A quaternary electrolyte BaCaNaLi shows promise for further improved MCFC life/performance and for reducing temperature sensitivity of Li/Na carbonate electrolyte.

APPROACH

We use a carbonate-wetted $LiAlO_2$ strip test to screen prospective electrolyte compositions for cation segregation and electrolyte migration. When the two cations have equal mobilities (the *Chemla Effect*), an electrolyte is considered nonsegregating and electrolyte migration should be minimized. As more convincing evidence of electrolyte performance, we test them in 100-cm^2 cells at 320 mA/cm^2.

PROJECT DESCRIPTION

We screened electrolyte compositions for segregating behavior by using 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. In our case, strips of carbonate-wetted $LiAlO_2$ (Cyprus-Foote) were made from cold-pressed powders (150 MPa). The strip was purged with a 1:2 O_2:CO_2 gas mixture (500 ml/min) at 655°C. After 72 h at 20 V, the potential distribution in the strip reached equilibrium. The strips were quenched under load and later examined by metallography. These strips were sectioned for chemical analysis by inductively coupled plasma/atomic emission spectroscopy (ICP/AES). From the ICP/AES results, cation ratios and electrolyte fill in each of the sections were calculated. The variation in cation composition vs. strip length was linear; therefore, these deviations were represented as a single cation separation value, or "segregation factor," given in terms of (m/o)/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 m/o 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.

Exploratory work with the quaternary Li/Na/Ca/Ba carbonate showed a suppression of melting point due to equilimolar addition of Ba/Ca to Li/Na electrolyte. Electrolyte compositions containing 2-10 m/o Ba/Ca additions were also evaluated for cation segregation.

Bench-scale (100-cm^2) MCFC tests using off-eutectic Li/Na electrolytes show increased performance at 160 mA/cm^2, as compared with the baseline cell containing the Li/Na eutectic composition. Increases in electrolyte lithium content from 52/48 to 71.5/28.5 Li/Na improved the cell potential by 75 mV. 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 m/o). 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 m/o Li improve cell performance over the 52/48 Li/Na eutectic that is commonly used.

Cell area-specific impedances, a combination of IR losses and electrode polarization, for the Li/Na electrolyte cell tests show a strong correlation with the segregation factor from the strip screening tests. This correlation suggests that the nonsegregating property of the carbonate and the composition of the carbonate at the electrodes play a significant role in the MCFC performance.

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 [6], but an apparent drawback is its greater temperature sensitivity [7].

We have identified a range of quaternary electrolyte compositions, Li/Na/Ca/Ba carbonates, which should yield general improvement of MCFC operation and performance. These improvements include high current-density operation (250-360 mA/cm^2), reduced temperature sensitivity, and anticipated extended life. Transfer of this technology to commercial developers will aid its adaptation.

RESULTS

The Strip "Gasket" Test

As previously described, we screen electrolyte compositions for nonsegregation using carbonate-wetted strips, which are submitted to 5 to 20 V potential gradients. After 72 h at 20V, the potential distribution in the strip has reached equilibrium. The strips were quenched under load and later examined by metallography. These strips were sectioned for chemical analysis by inductively-coupled atomic emission spectroscopy (ICP/AES). Here, 2-g samples were removed from several regions along the 12-cm strip length. From the ICP/AES results, cation ratios and electrolyte fill in each of the spots were calculated.

Based on the published Li_2CO_3-Na_2CO_3 phase diagram, we chose the 52/48 m/o Li/Na eutectic composition as a baseline for the study. Figure 1 shows the ICP/AES results of samples taken at specified positions on the strips. The 52/48 Ni/Na results are compared with those of the 67/33 Li/Na composition. The variation in cation composition vs. strip length was linear; therefore, these deviations were represented as a single cation separation value or segregation factor given in terms of (m/o)/cm.

The ICP/AES results are presented in a plot of electrolyte segregation factor vs. Ca/Ba carbonate composition (see Fig. 2). The plot shows that the nonsegregating range is 67-75 m/o Li. Surprisingly, the eutectic 52/48 m/o Li/Na carbonate displays the greatest cation segregation. Even on the Na-rich side of the eutectic composition, 40/60 Li/Na carbonate exhibits lower cation segregation than does the eutectic.

The trend in electrolyte fill vs. 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 [8]. Indeed, post-test examinations of bench-scale Li/Na cell tests have shown flooded cathodes.

The quaternary BaCaNaLi carbonates (5% and 3%) were also examined in strip tests. Cation composition vs position in the test strips is presented in Fig. 3. For both compositions, a small degree of cation segregation is apparent, with Ba/Ca concentration increasing at the positive end of the strip. The 3% BaCaNaLi is very close to a nonsegregating electrolyte with approximately 90% of the strip consisting of the starting BaCaNaLi composition.

Bench-scale Cell Tests

Bench-scale 10 x 10-cm MCFC tests were assembled with standard Ni anodes (6% Cr) and Ni cathodes. The electrolyte tiles were formed by hot-pressing. The anode wet seal was aluminized with aluminum foil. Six Li/Na compositions and five BaCaNaLi compositions in m/o (10,5,4,3, and 2 Ba/Ca) were tested. All cells were operated for at least 500 h at 650°C. To investigate the electrolyte segregation phenomenon, the cells were operated at least 320 mA/cm^2 for at least 1/2 h at the end of the life test. The cells were rapidly quenched to fix compositional gradients. Metallographic and chemical analysis were used to determine composition and amount of carbonate in the MCFC components.

Performance data of the bench-scale tests were used to compare the performance of Li/Na electrolyte compositions. Data on cell impedance, cell voltage, electrode performance at various utilizations and current density operations were collected as a function of time at 1 atm with laboratory standard oxidant (air + 28% CO_2) and humidified fuel (80%H_2 + CO_2).

Figure 4 shows the polarization behavior of 6 MCFC cell tests using Li/Na electrolyte compositions. These tests were conducted with fuel and oxidant utilizations of 60% and 40%, respectively, at 320 mA/cm^2 and 650°C. Cell area-specific impedances, a combination of IR losses and electrode polarization, for Li/Na electrolyte cell tests are shown in Fig. 5. The cell tests displayed improved performance as the electrolyte composition approached the nonsegregating range. Compared to the baseline 52/48 carbonate composition, MCFC voltage increased about 100 mV at 160 mA/cm^2 for the off-eutectic Li/Na carbonate electrolyte compositions, 65-75 mol% Li_2CO_3.

High current density operation in Li/K carbonate cells leads to early cell shorting [9]. Electrolyte segregation phenomena or electrolyte freezing presents problems for high current-density operation. The 71.5/28.5 Li/Na composition exhibited a cell potential of 0.76 V at 320 mA/cm^2, but this appears to be the upper limit of improved cell performance due to higher Li content electrolytes. The cell performance of the 75/25 Li/Na electrolyte composition (0.71 V at 320 mA/cm^2), although still much improved compared to the 52/48 LiNa, is lower than that of the 71.5/28.5 Li/Na electrolyte cell. Nonetheless, these cell tests suggest electrolytes in the composition range of 65-75 m/o Li improve cell performance over the 52/48 Li/Na eutectic that is commonly used.

We find an apparent correlation between improved MCFC performance and nonsegregating electrolyte compositions. The polarization behavior of 6 MCFC cell tests using Li/Na electrolyte compositions is taken from Fig. 5. These tests are conducted with fuel and oxidant utilizations of 60% and 40%, respectively, at 320 mA/cm^2 and 650°C. As in Fig. 3, these deviations were represented as a single cation separation value or segregation factor, given in terms of (m/o)/cm. Cell area-specific impedances, a combination of IR losses and electrode polarization, for Li/Na electrolyte cell tests are now correlated with a segregation factor from the strip screening tests (see Fig. 6). This correlation suggests that the composition of the carbonate at the electrodes plays a significant role in the MCFC performance. Only a minor portion of the reduced cell polarization can be attributed to increased electrolyte conductivity that is associated with the increased Li_2CO_3 content of the nonsegregating Li/Na composition. Post-test examination of MCFC cell tests will investigate this observation in support of our continued electrolyte development work.

APPLICATION

The quaternary carbonate electrolyte Ba/Ca/Na/Li combines a nonsegregating property with a reduced melting point. Differential thermal analysis (DTA) shows a 100°C lower melting point for the BaCaNaLi electrolytes (450°C) than the Li/Na carbonate eutectic.

The results of 10 x 10-cm MCFC test with quaternary BaCaNaLi carbonate electrolytes showed a prospect for reduced temperature operation (Fig. 7). These cells displayed stable cell potentials for more than 1000 h at 160 mA/cm^2 (60/40 % fuel/oxidant utilization). Cell performance and polarization curves were taken under conditions similar to those of the 52/48 Li/Na carbonate cell. The five cells were operated over a temperature range of 550-700°C to establish performance vs. temperature characteristics. Although not shown, the baseline 52/48 Li/Na and 10% BaCaNaLi have very similar temperature characteristics. At 550°C, the 3% BaCaNaLi carbonate cell had a stable voltage 75 mV greater than that of the baseline 52/48 Li/Na. At 550°C, the 2% BaCaNaLi carbonate cell exhibits a 25 mV improvement. Unlike some of the earlier quaternary BaCaNaLi carbonate electrolytes, both 2% and 3% BaCaNaLi could be operated at 320 mA/cm^2. The quaternary 3% BaCaNaLi carbonate electrolytes shows promise for improved cell stability at 320 mA/cm^2 and a 50-75°C lower operating temperature.

FUTURE WORK

Future work will concentrate on life testing of bench-scale MCFCs for a selected range of quaternary electrolyte compositions. We will continue our investigation of the carbonate composition at the electode/electrolyte interface with postoperative analysis. The primary focus will be to develop MCFCs with advanced quaternary compositions to learn how they affect MCFC performance. The next step in our advanced electrolyte development is to provide the physical properties to assist with the MCFC design (i.e, wetting properties for proper electrode microstructure development). To facilitate DOE-contractor adaptation of our electrolyte, we are modifying our MCFC testing to accommodate tape-cast components. Having comparable MCFC tests will aid us in addressing specific application details.

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REFERENCES

1. H. R. Kunz, "Transport of Electrolyte in Molten Carbonate Fuel Cells, "J. Electrochem. Soc., 134 (1987) 105.
2. Y. Miyazaki, *et al.*, "Alternative Electrolyte Compositions for MCFC," Proc. 3rd Int. Symp. on Molten Carbonate Fuel Cells, Vol. 93-3, The Electrochemical Society, NJ, 1993, p. 444.
3. E. Pigeaud, *et al.*, "Determination of Electrolyte Composition for MCFC," Final Report to DOE, Contract No. AC21-86MC23264, June, 1989.
4. K. Ota, *et al.,*"Solubilities of Materials for MCFC," Proc. Int. Fuel Cell Conference, Makuhari, Japan, 1992, p. 165.
5. E. T. Ong, et al., "Cell Testing of Li/Na Electrolyte," Proc. 1994 Fuel Cell Seminar, San Diego, CA, 1994, p. 404.
6. R. C. Makkus, E. F. Sitters, P. Narmensma, and J. Huijsmans, "MCFC Electrolyte Behavior Li/K vs. Li/Na Carbonate," Carbonate Fuel Cell Technology IV, ed. J. R. Selman, *et al.*, p. 344-352, Vol. 97-4, Electrochem. Soc. (1977).
7. C. Sishtla, R. Donado, E. Ong, and R. Remick, "Temperature Sensitivity of MCFCs Using Lithium/Sodium Electrolyte,"Carbonate Fuel Cell Technology IV, ed. J. R. Selman, *et al.*, p. 315-328, Vol. 97-4, Electrochem. Soc. (1977).
8. Th. Brenscheidt, O. Bohme, and H. Wendt, "Mass Transfer and Steady State Concentration Distributions of Binary Electrolytes and Additives in MCFCs," Molten Salt X, ed. R. T. Carlin *et al.*, Vol. 96-7, Electrochem. Soc. (1996)
9. H. R. Kunz and L. J. Bregoli, "Ionic Migration in MCFC," Proc. 2nd Int. Symp. on MCFC Technology, The Electrochemical Society, Vol. 90-16, NJ, 1990, p. 157.

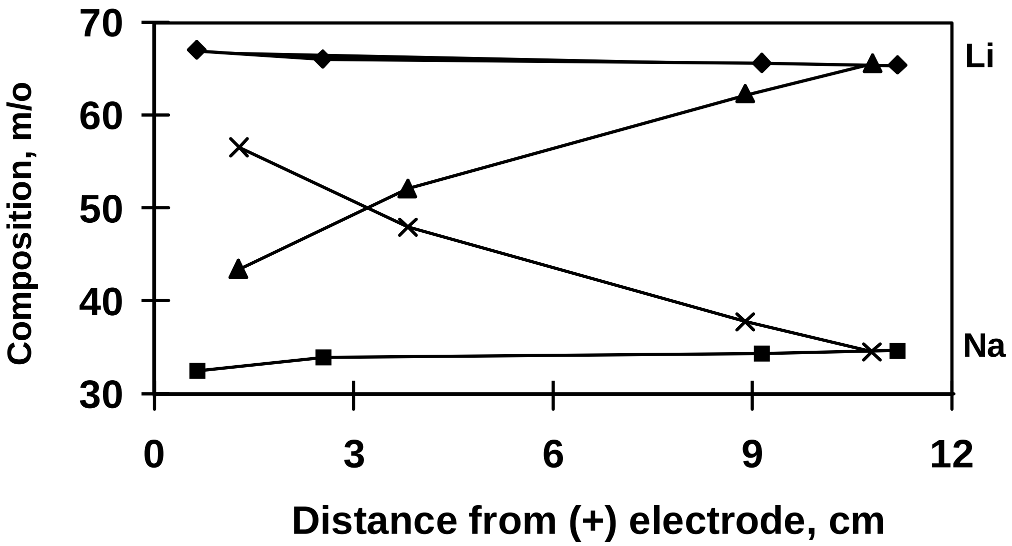


Fig. 1. **Fully-developed cation composition distribution of 12-cm-long strips (with 20V applied) for two Li/Na carbonate compositions: 52/48 and 67/33.**

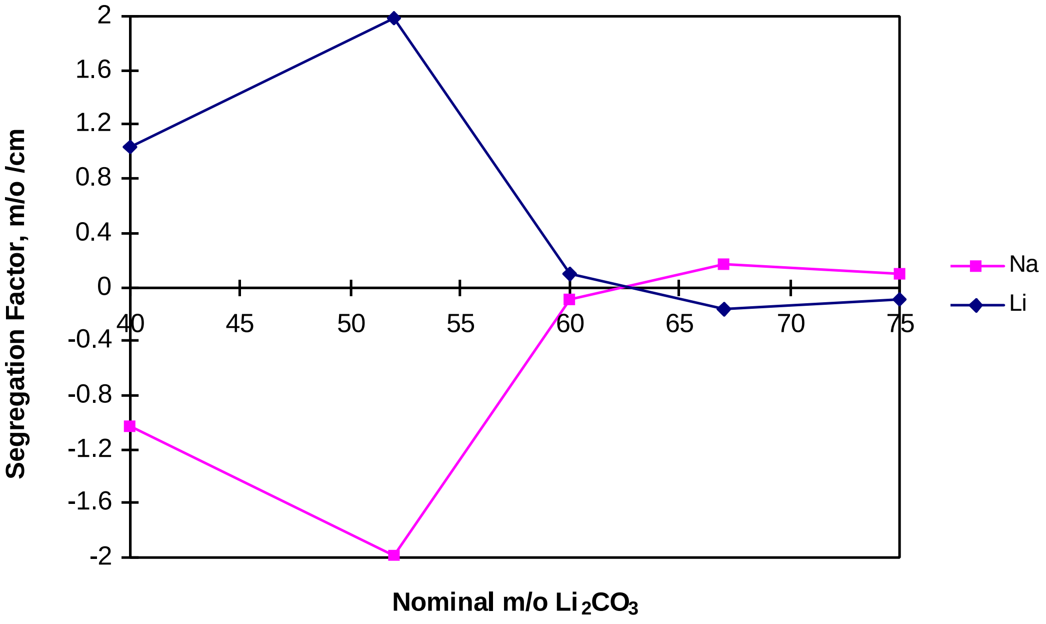
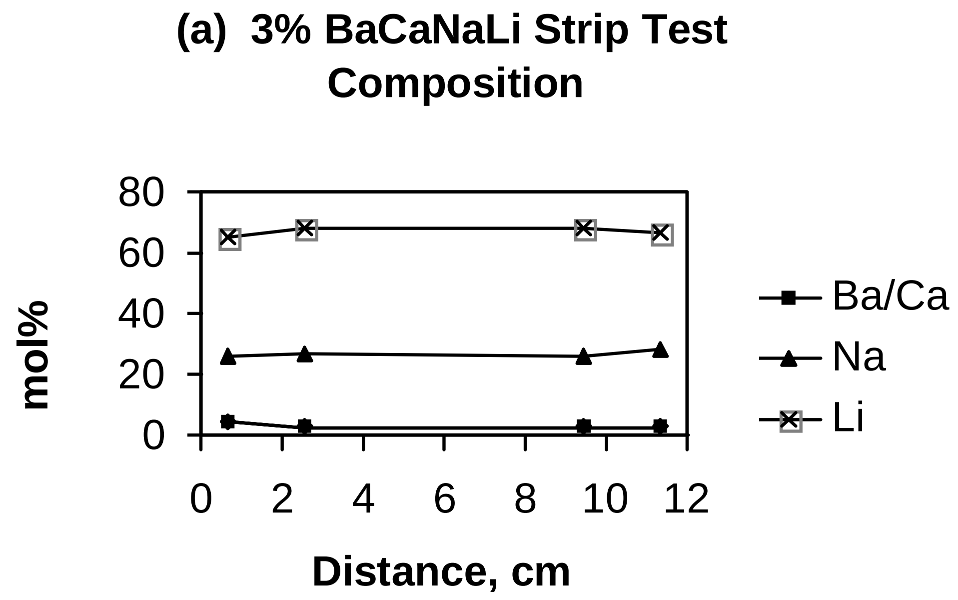


Fig. 2. **Segregation factors versus composition for a range of Li/Na carbonate electrolytes.**



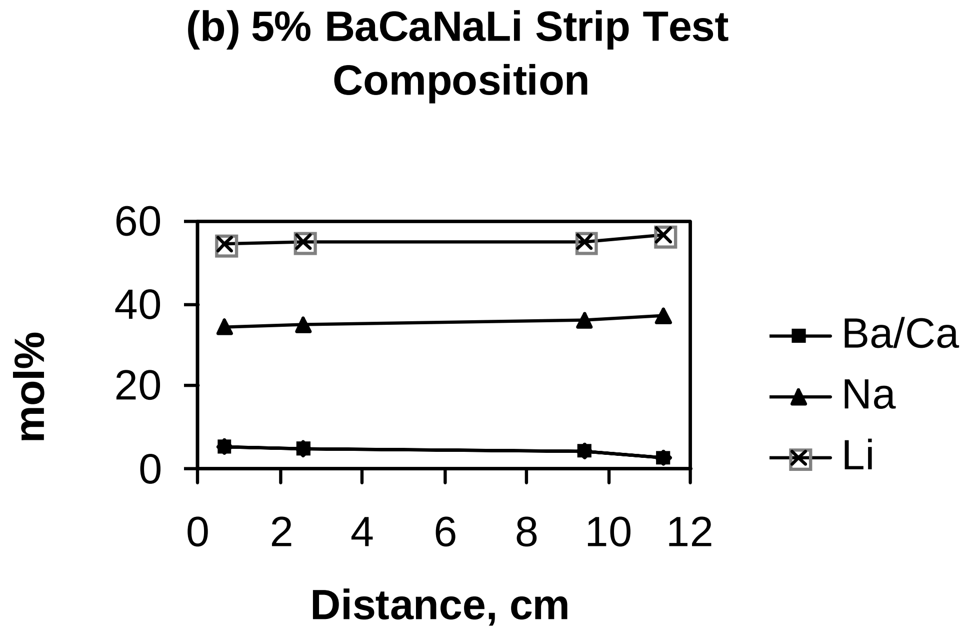


Fig. 3. Fully-developed cation composition distribution of 12-cm-long strips (with 20 V applied); with (a) 3% BaCaNaLi (3/3/28/66 m/o carbonate) and (b) 5% BaCaNaLi (m/o 5/5/38/52 carbonate) electrolyte.

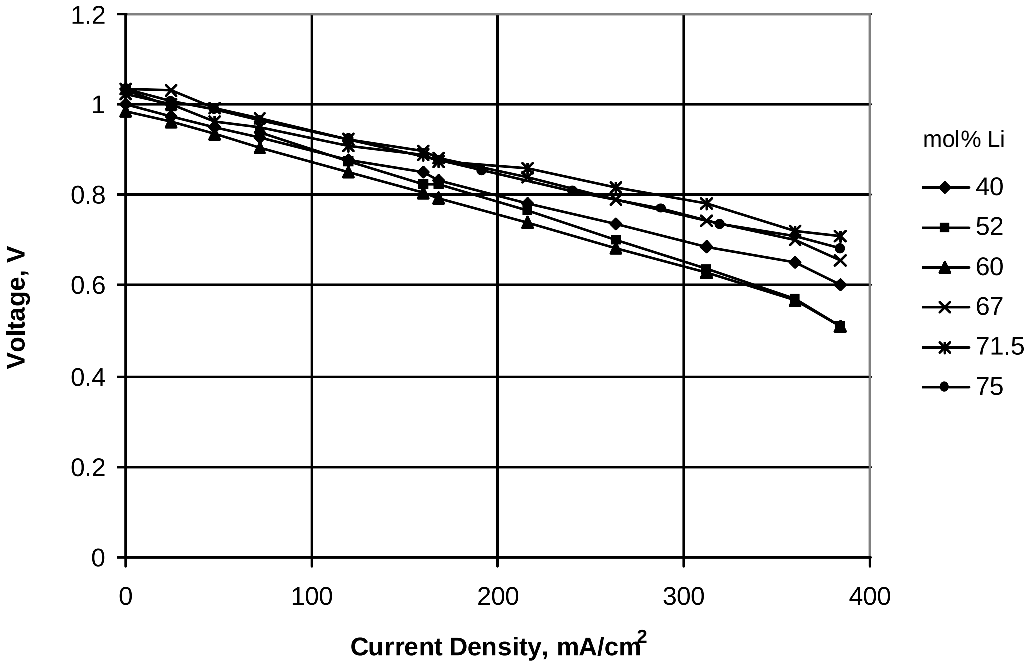


Fig. 4. **Polarization curves indicating cell impedance as related to electrolyte composition: 6 Li/Na compositions (in m/o) 40/60, 52/48, 60/40, 67/33, 71.5/28.5 and 75/25.**

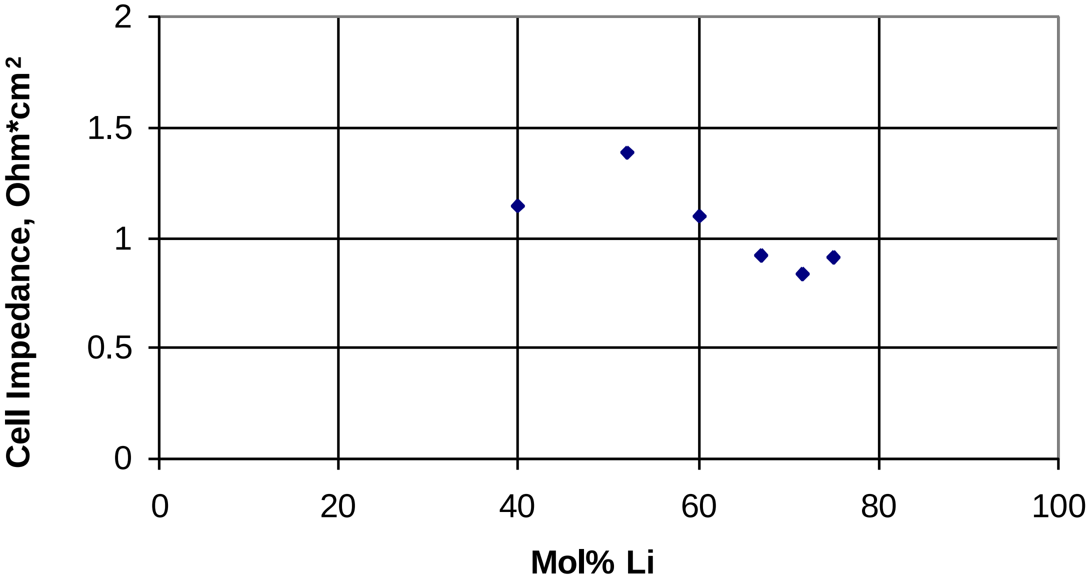


Fig. 5. **Cell impedance as related to electrolyte composition: 6 Li/Na compositions (in m/o) 40/60, 52/48, 60/40. 67/33, 71.5/28.5 and 75.25.**

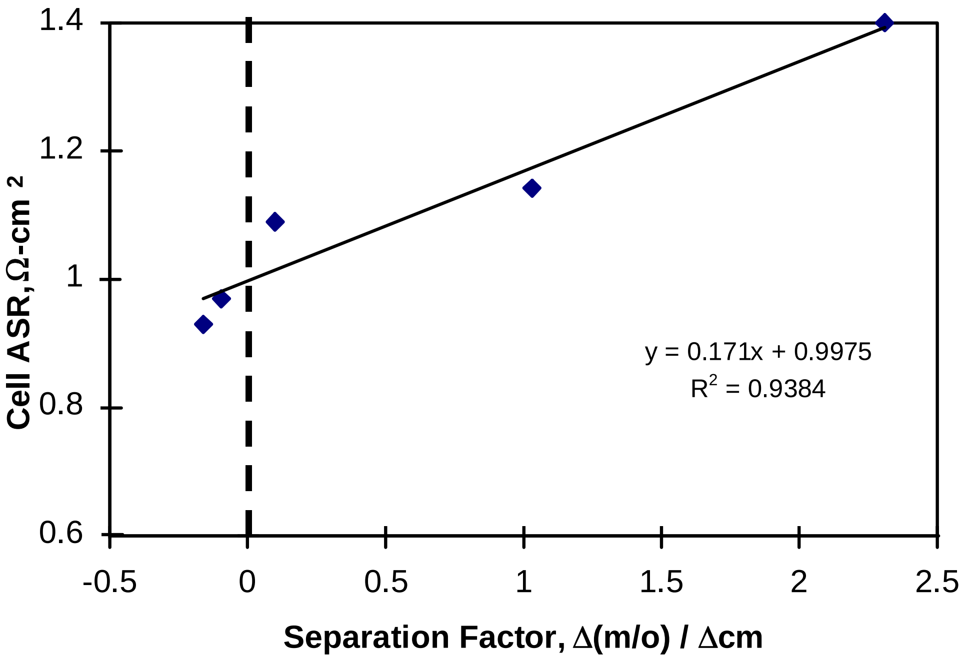


Fig. 6. **MCFC cell impedances for range of Li/Na carbonate composition: (40/60 to 75/25 mol%) compared to separation factors established from our strip segregation-screening tests.**

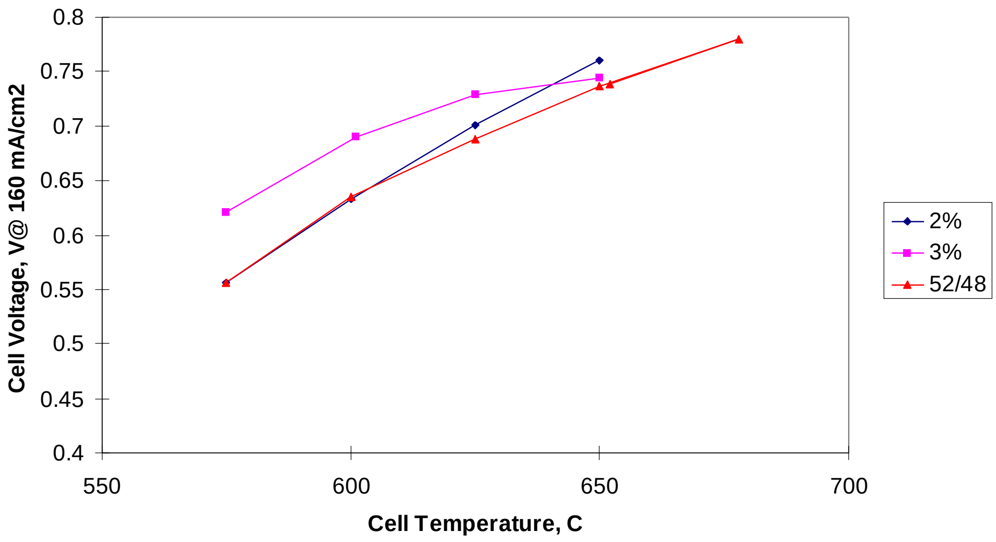


Fig. 7. **Temperature sensitivity of three MCFCs having various electrolyte compositions: 2% and 3% BaCaNaLi, along with baseline 52/48 Li/Na carbonate. Cells operated under standard conditions at 160 mA/cm^2.**