

Non-Segregating Electrolytes for Molten Carbonate Fuel Cells

by

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Introduction

In the current technology, molten carbonate fuel cells (MCFCs) employ a Li/K carbonate mixture. The mixture, usually 62 m/o Li_2CO_3 and 38 m/o K_2CO_3 , melts below about 550°C and, when mixed with lithium aluminate, serves as both the electrolyte and gasketing for the cell and stack. Electrolyte segregation has been reported to occur within both the cell and the 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 that, in turn, leads to severe performance decline of the "end" cells.

Objective

Argonne National Laboratory (ANL) is developing molten carbonate electrolyte compositions that have minimal segregation in the molten carbonate fuel cell (MCFC) and stack electric field. 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 alkaline earth carbonates. Segregation properties are examined in "gasket"-strip (20-V) screening studies, as well as in 100-cm^2 cell tests.

Approach

ANL is exploring Li-Na carbonate electrolyte compositions that have minimal segregation in the MCFC and stack under load. The segregation/migration characteristics of the electrolyte under load are determined and modified. The liquidus composition range of the Li-Na carbonate electrolyte is broader than that of the Li-K carbonate electrolyte, which aid fuel cell operation. In

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addition, the Li-Na carbonate electrolyte embodies a number of attractive features for MCFC advancement:

- It is more conductive than the Li-K carbonate electrolyte [1]
- It may lead to longer life due to lower Ni^{2+} solubility [2]
- Corrosion rates for hardware components are lower in the Li-Na carbonate electrolyte [3], and
- It has no volatile, potassium-containing constituents.

Project Description

A screening test for electrolyte segregation was developed that was based on an earlier method by Kunz [4] in which carbonate-wetted strips were subjected 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 contained eight gold probes spaced regularly along its length and Ni electrode strips at each end to apply the voltage. At 650°C , a potential of about 20 V was applied across a 10-cm-long bar of material containing electrolyte and LiAlO_2 . Measuring voltage drops along the length of the strip was used to gauge electrolyte content and composition. This assembly was held between two alumina plates (held in compression by a Belleville spring washer) that also formed the gas-flow channels. The strip was purged with a 2:1 O_2 to CO_2 gas mixture (500 mL/min) at $655\pm 10^\circ\text{C}$.

The effects of cell chemistry on Li-Na carbonate electrolyte segregation were investigated in 10×10 -cm cell tests. Electrolyte tiles containing selected carbonate compositions were prepared and tested at 650°C in cells containing standard Ni cathodes and anodes, unlike the studies by other developers of MCFCs with Li/Na electrolytes [5]. After an initial conditioning period of at least 500 h and under laboratory-standard oxidant, the current density in the cells was increased to at least 250 mA/cm^2 . The cells were quenched under electric load to maintain electrolyte constituent distribution.

Results

Strip "Gasket" Test. The fully-developed potential distributions after 72 h at 20 V from the strip tests with the four Li/Na carbonate compositions was obtained, Fig. 1. Composition (a) is a near eutectic composition of Li/Na carbonate. The potential distribution of off-eutectic Li/Na carbonate compositions equilibrate with less voltage variation than for composition (a). The strip samples were quenched under load and later examined by metallography. The trend is clear; the fully developed potential distribution becomes more uniform as Li/Na ratio is distanced from the eutectoid composition. Composition (c) provides the least electrolyte segregation. These strip samples were mounted in epoxy to permit sampling for chemical analysis. We are unable to determine Na content with energy-dispersive spectroscopy (EDS). An inductively coupled plasma/atomic emission spectroscopy (ICP/AES) analysis of these strip elements is under way to further support the non-segregating characteristics that have been determined from cell tests.

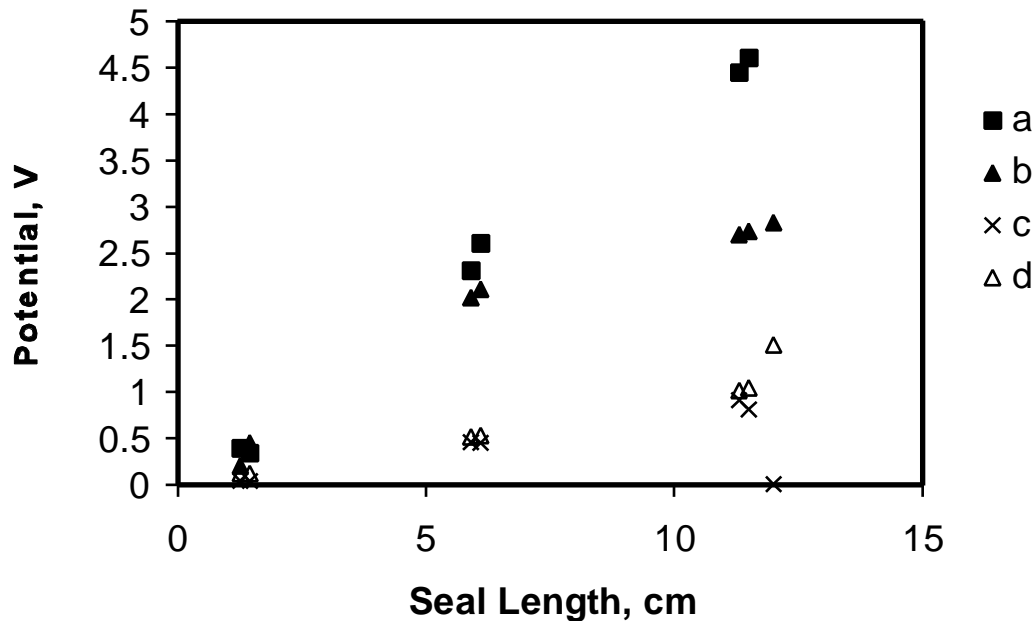


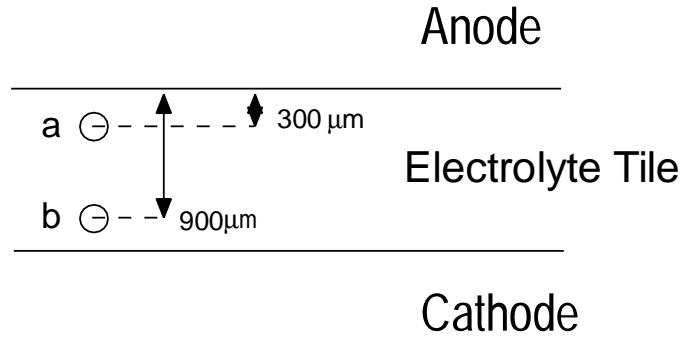
Figure 1. Fully developed potential distribution of 12-cm-long strips (20 V applied) for four Li/Na compositions.

Bench Scale Cell Tests. Bench scale, 10×10 -cm MCFC tests were assembled with standard Ni anodes (6% Cr) and Ni cathodes. The electrolyte tile was formed by hot-pressing. The anode wet seal was aluminized with aluminum foil. Four Li/Na carbonate compositions were tested. All cells were operated for at least 500 h at 650°C . For the purposes of investigating the electrolyte segregation phenomenon, the cells were operated at 400 mA/cm^2 for at least 0.5 h at the end of the life test. The cells were rapidly quenched to fix compositional gradients. Metallographic and analytical methods (secondary ion mass spectroscopy [SIMS]) are 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 operation 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). The Li/Na composition did affect the polarization curves of these four cells. These tests were conducted with fuel and oxidant flows for 60% and 40% utilizations, respectively, at 320 mA/cm^2 and 650°C . Independent from the strip test, performance improved as non-segregating electrolyte property was enhanced. By comparison, high current density operation in Li/K carbonate cells leads to early cell shorting [6]. An electrolyte segregation phenomenon or electrolyte freezing would present problems for high current density operation. This phenomenon is not seen for the non-segregating Li/Na composition.

Post-Test Observations in 100 cm^2 Cells. The SIMS analysis for Li/Na was conducted on electrolyte tile cross sections of two 10×10 cm MCFC test cells, Fig. 2. Cell 2 has the eutectic Li/Na carbonate composition. The object of this analysis was to examine cation segregation across

the electrolyte subsequent to the quench of the cell. Based on two point values, anode/cathode, the off-eutectic deviation of the Li and Na content was suppressed with the Li/Na ratio exhibiting lesser electrolyte segregation in our strip tests. These results substantiate the findings of both the strip test and the cell performance at high current density for the development of non-segregating electrolytes.



Cell No.	a/b Ratio for Li	a/b Ratio for Na
1	2.3±0.9	1.8±0.4
2	8.9±2.1	1.2±0.3

Figure 2. Position-related Li- and Na-cation ratio by SIMS analysis for the cross sections of two test cells having different Li/Na compositions.

Future Activities

With our progress in Li/Na evaluations, we have developed a baseline for examining other electrolytes. We will continue with the strip-element tests to include alkaline-earth carbonates. Cell tests will target long-term, high-current operation as a further indication of a non-segregating electrolyte.

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