Supporting R&D of Industrial Fuel Cell Developers

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Abstract
Argonne National Laboratory is supporting the industrial developers of molten carbonate fuel cells (MCFCs) and tubular solid oxide fuel cells (SOFCs). Our results suggest that a lithium concentration level of 65-75 mol% in the Li/Na electrolyte will improve cell performance. We have made inroads in understanding the interfacial resistance of bipolar plate materials, and we have reduced the air electrode overpotential in SOFCs by adding dopants.

Introduction
Argonne National Laboratory (ANL) is supporting the industrial developers of molten carbonate and tubular solid oxide fuel cells in the areas of (1) nonsegregating electrolytes, (2) interfacial resistance of bipolar plate materials, and (3) overpotentials at the air electrode. This presentation covers progress in these three areas.

Nonsegregating Electrolytes
Differences in the ionic mobility of the lithium and potassium ions in the $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ have long been known to lead to changes in composition between the positive and negative side of the fuel cell (1). As a result, the melting point and other physical properties of the electrolyte can vary at different locations in the fuel cell. To eliminate these effects, ANL has been exploring nonsegregating electrolyte compositions.

We screen electrolyte compositions for nonsegregation using 12-cm-long strips, which are wetted with carbonate and exposed to 5- to 20-V potential gradients. These conditions simulate the gasketing strip of an externally manifolded molten carbonate fuel cell (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
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metallography. They were sectioned and analyzed by inductively coupled plasma/atomic emission spectroscopy (ICP/AES). From the ICP/AES results, cation ratios and electrolyte fill in each section were calculated. The variation in cation composition vs. strip length was linear; therefore, these deviations were represented as a single cation separation value or a "segregation factor," given in terms of (mol%)/cm.

The ICP/AES results of electrolyte segregation were correlated with the Li/Na carbonate composition. Figure 1 shows the separation factors of Li and Na for $40$ to $75\%$ lithium as measured by the strip test technique. Segregation is fairly substantial at the eutectic composition of $52\%$ Li, but minimal between $60$ and $75\%$. Even the Na-rich side of the eutectic composition, $40/60$ Li/Na carbonate, exhibits lower cation segregation than does the eutectic.

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, we were able to lower the melting point and maintain nonsegregating behavior (See Fig. 2).

To explore the relation between electrolyte composition and electrochemical behavior in the fuel cell, we ran cell tests for various Li/Na compositions (Fig. 3) and for the ternary electrolytes (Fig. 4). Bench-scale (100-cm$^2$) MCFC tests using off-eutectic Li/Na electrolytes show increased performance at $160$ mA/cm$^2$, 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 (in mol%): $40/60$, $52/48$, $60/40$, $67/33$, $71.5/28.5$, and $75/25$. The results show a strong correlation between nonsegregating characteristics and improved cell performance. These cell tests suggest that electrolytes in the nonsegregating composition range of $65–75$ mol% Li improve cell performance over the $52/48$ Li/Na eutectic that is commonly used.

It is evident that cell potentials increase with lithium content in the binary electrolytes, and that the potentials are higher in the quaternary than in the binary eutectic mixture. At this point we are not certain whether the improvement in cell potential is caused by higher electrolyte conductivity or lower overpotentials, but we have ascertained the stability of the cell potentials over at least two thousand hours. Remarkably, the potentials remain stable, even at current densities of $240$ mA/cm$^2$.

**Interfacial Resistance of Bipolar Plate Materials**

The resistance of the oxide layer on the cathode side of the bipolar plate diminishes MCFC performance and may cause a significant voltage loss. Approximately $25\%$ of the internal cell resistance could be attributed to the oxide layer on the stainless steel. Others (2,3) have assessed the corrosion behavior of commonly used stainless steels and of proprietary alloy compositions. Type 310 stainless steel (SS) exhibits a $50\%$ lower rate of corrosion but the resulting oxide scales have a higher electrical resistance than does Type 316L ($200-250$ mΩcm$^2$ versus $25$ mΩcm$^2$ respectively). The lower resistance of the oxide scale of Type 316L SS makes it preferable to Type 310 SS for the MCFC.
At ANL, we are attempting to identify the relations and trade-offs between corrosion protection and electric resistance, with the objective of finding a better solution than is currently available. Our approach is to analyze the oxide layers on the steels after certain exposure times to correlate the composition of the layers with that of the base metal, and to measure oxide scale electrical resistances.

The electrical resistivity was measured in a cathodic environment (30% CO₂/air). A specially designed furnace examines 12 samples at once. A HP4338A milliohmimeter, which uses a 4-wire measurement at 1 kHz, monitors the resistance of the 1.5- X 1.5-cm specimens. The samples were placed on an Al₂O₃ disk and connected with gold wires in series. Other investigators (2,3) have observed that the oxide scale electrical resistance of Type 316L stainless steel fluctuates with time (50-100 mΩcm²). Periodically (about every 750 hrs), some of the samples were removed from the furnace to determine the microstructural composition of the formed oxide layers. Scanning electron microscopy (SEM) reveals that as buckling occurs between inner and outer oxide scale layers, gaps develop which disappear as the scale continues to grow. On NKK, the corrosion layers are very thin. But the base metal near the surface becomes porous, and the oxide scale resistance increases to 150-200 mΩcm².

Figures 5, 6, and 7 show cross sections for Type 316L SS, Type 310 SS, and NKK Ni-Cr alloy. We use a combination of x-ray diffraction (XRD) and SEM/energy dispersive x-ray spectroscopy (EDAX) to determine oxide scale composition. Oxide scale layers are examined by systematically polishing through the oxide scale. The outer layer is LiFeO₂ in all cases. On Type 316L SS, LiFe₂O₃ is found near the base metal, with an as-yet-unidentified layer in the middle. This intermediate layer appears to impede the diffusion of oxygen. On Type 310 SS, the oxide scale close to the metal is LiCrO₂. On NKK, the corrosion layers are very thin 10-15 microns. The oxide scale close to the metal is also LiCrO₂, but the metal near the surface is porous. Future work will attempt to clarify the roles of these layers.

Air Electrode Overpotentials

The air electrode overpotential in solid oxide fuel cells (SOFCs) is about 60 mV. Cutting it in half would improve the system efficiency by nearly five percent. Previously, we have shown that the principle reason for the overpotential is the lack of oxide ion conductivity in the lanthanum manganite air electrode material. This problem can be overcome by mixing the lanthanum manganite with a good ionic conductor such as yttrium-doped zirconia or by finding ways to introduce more oxide ion conductivity into the manganite. ANL has chosen the second option and has explored using dopants on the "B". Figure 8 shows a plot of overpotential versus dopant concentration as determined by half-cell measurements. The overpotential is clearly minimized with a five percent dopant concentration.
Acknowledgment


References


Fig.1. Segregation factors vs. composition for a range of Li/Na carbonate electrolytes
Fig. 2. Fully-developed cation composition distribution on 12-cm-long strips of Li/Na carbonate with and without Ba/Ca addition 20V applied.
Fig. 3. Polarization curves indicates cell impedance is related to electrolyte composition: 6 Li/Na compositions (in mol %) 40/60, 52/48, 60/40, 67/33, 71.5/28.5, and 75/25.
Fig. 4. Polarization curves indicates cell impedance is related to electrolyte composition: eutectic Li/Na and three levels of Ba/Ca additions to Li/Na carbonate.
Fig. 5. Development of oxide scale on Type 316L Stainless Steel: (a) SEM cross section and (b) XRD of scale thickness at increasing exposure times
Fig. 6. Development of oxide scale on Type-310 Stainless Steel:
(a) SEM cross section and (b) XRD of scale thickness at 800 h exposure time
Fig. 7. Development of oxide scale on NKK Ni/Cr alloy: (a) SEM cross section and (b) XRD of scale thickness at 1500 h exposure time
Fig. 8. Overpotential versus dopant concentration as determined by half cell measurements.