ON THE TECHNOLOGICAL STATUS OF MOLTEN CARBONATE FUEL CELLS

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ABSTRACT

Molten carbonate fuel cells (MCFCs) are presently under development for electric utility power generation. Much progress has been made in the MCFC technology during the last ten years. This paper examines and summarizes the technological status of the MCFC. Emphasis is placed on discussion of technical issues such as cathode dissolution corrosion, electrode deformation, electrolyte loss, sulfur contamination, and internal reforming. A brief discussion of the importance of electrolyte basicity in MCFCs is also given.

INTRODUCTION

The molten carbonate fuel cell (MCFC) represents one of the most important applications of molten salts. The fuel cell employs molten carbonates as the electrolyte. Carbonate mixtures are the only electrolytes which are invariant with respect to the electrochemical combustion of hydrogen and carbon monoxide, thus providing the basis for the fuel cell. The overall reactions are as follows:

Anode: \[ \text{H}_2 + \text{CO}_3^{2-} = \text{H}_2\text{O} + \text{CO}_2 + 2e \]  
\[ \text{CO} + \text{CO}_3^{2-} = 2\text{CO}_2 + 2e \]  
Cathode: \[ \frac{1}{2}\text{O}_2 + \text{CO}_2 + 2e = \text{CO}_3^{2-} \]

The state-of-the-art MCFC consists of a porous stabilized nickel anode (fuel electrode) and a porous lithium-doped nickel oxide cathode (oxidant electrode), separated by a lithium aluminate matrix filled with lithium and potassium carbonates (62–70 mol% Li$_2$CO$_3$) as the
electrolyte. The cell is operated at a temperature of about 925 K and at a pressure of 1 to 10 atm; the fuel gas is a humidified mixture of H₂ and CO, and the oxidant is a mixture of O₂ and CO₂ which may contain water vapor.

Present MCFC designs are based on a planar geometrical configuration. Practical electrical power generation is achieved by stacking a series of cells to build voltage. A bipolar plate carries electrons from the anode of one cell to the cathode of the next in electrical series. The essential components of a MCFC stack is shown in Fig. 1.

The MCFC operating temperature (about 925 K) is high enough to produce valuable waste heat. The waste heat can be used to supply heat for bottoming cycles and/or cogeneration purposes (process or space heat). In an MCFC power plant using natural gas fuel, the most important process heat use will be for the reforming of methane. For MCFCs, internal reforming of methane is possible (i.e., the waste heat is directly available within the fuel cell for the conversion of methane directly to hydrogen and carbon monoxide in a driven reforming reaction in the anode region of the fuel cell). The internal reforming capability of the MCFC offers higher system efficiencies.

The MCFC, following a very intensive development effort during the last ten years, may be approaching the threshold of commercialization. The MCFC market includes electric utility, cogeneration, and on-site applications. This paper examines and summarizes the technological status of the MCFC. A brief discussion of the importance of electrolyte basicity in MCFCs is also given.

TECHNOLOGICAL STATUS OF MOLTEN CARBONATE FUEL CELLS

Commercial MCFCs are expected to range in cell area from 0.37 to 1.5 m² (4 to 16 ft²). The number of cells per stack is expected to range from 75 to 700, giving a total stack height range of 0.46 to 5.1 m (18 to 200 inches). An electrical generating plant will contain one or more of these stacks, each of which will have an output of 5 kW to 1 MW (1). Recent MCFC developments in the U.S. are focused on stack design and operation and development of a fundamental understanding of reactions, materials, kinetics, and processes in an operating fuel cell. Although there are as yet no stacks in operation of the size envisioned for commercialization, results on subscale stacks [20 cells with 930 cm² (1 ft²)/cell] are very encouraging. A subscale stack was operated for 5000 h (1).
The average cell performance of the stack met prediction and duplicated the single cell data (Fig. 2) (2). Testing of an 0.74-m² (8-ft²) short stack (20 cell) is in progress (2). Several major technical issues have been identified, and the status of each of these issues is discussed below.

* Cathode dissolution: The instability of NiO during cell operation is now considered one of the major technical difficulties facing MCFC development (3). Nickel oxide has a small degree of solubility in the carbonate electrolyte in the fuel cell cathode environment (about 10-15 ppm). However, the dissolved nickel ions diffuse, under a concentration gradient, from the cathode toward the anode. At some location between the two electrodes and under the influence of reducing conditions caused by the anode gas, the dissolved nickel precipitates as nickel metal. The precipitation of nickel creates a sink for the nickel ions, which facilitates further NiO dissolution. Thus, the dissolution of NiO can be a major life-limiting factor for the MCFC. The present industrial efforts attempt to prolong NiO life by employing low partial pressure of CO₂ and high-Li₂CO₃ electrolyte. Additives (e.g., MgO) to the carbonate electrolyte to lower NiO dissolution are also attempted. Although the lifetime of NiO can be extended under those conditions, it is not clear whether lowering the CO₂ partial pressure or changing other operating conditions will make the NiO cathode endure 40,000 operating hours required for commercial applications. Alternative cathode materials are being developed. Two materials, LiFeO₂ and Li₂MnO₃, have been identified as potential MCFC cathode materials. These materials were extensively tested and meet the requirements of stability, low solubility, and nonmigration. Adequate conductivities under realistic cell conditions can be achieved by doping the materials (4,5). The emphasis has now shifted toward fabricating appropriate cathode microstructures with doped materials, then testing them in cells (5).

* Corrosion: Another important question being addressed in MCFC technology concerns resistance to corrosion of current collectors/bipolar plates. In MCFCs, the bipolar plates are coated with a thin film of molten carbonate electrolyte and in contact with the cathode and the oxidant gas on one side and with the anode and fuel gas on the other side. They are therefore susceptible to hot corrosion attack (6,7). Corrosion of bipolar plates causes decline in cell performance and can lead to cell failure by allowing direct reaction of oxidant and fuel. The 316 stainless steel (SS) specified in the past for bipolar plates in laboratory cells was found not to be suitable for full-scale cells which have a life goal of 40,000 h.
Severe attack of the bipolar plate made of 316 SS, especially the anode side of the plate, was frequently observed in cells operated for a few hundred to a few thousand hours (8). Nickel cladding for protecting the anode side of 316 SS was attempted (8-10). However, there was still significant amount of corrosion on the cathode side of the plate. Corrosion and cell tests with 310 SS and INCO 825 indicated that plates made of these materials had better corrosion resistance in the fuel cell environment. These materials, however, did not show sufficient corrosion resistance to meet endurance goals on the anode side. In current MCFC stack tests, plates made of 310 SS or INCO 825 are nickel-coated on the anode side for corrosion protection. At present, a satisfactory bipolar plate material has not yet been identified.

* Electrode deformation: In MCFCs, the anode and cathode structures should be dimensionally stable. Any compaction of the structures not only decreases the active surface area but also may cause loss of contact and high resistances between components. Compaction may also cause significant tolerance requirements for stack hardware design. The porous nickel anode sinters at the cell operating temperature and compresses somewhat as a result of the cell holding force. Nickel anodes have been stabilized by dispersing small amounts of certain oxides such as chromia and alumina in nickel. Stack tests verified that the anode compaction goal has been attained with this stabilization method (1). Metal-coated ceramic anodes with good compaction resistance are also being developed (1). Recently, with the advent of dimensionally stable anodes, the compaction of the NiO cathode has been observed. For example, the average compaction of NiO cathodes in one stack test was found to be approximately 0.09 mm (3.5 mils) per cell (cell thickness of about 2.54 mm or 100 mils) (11). This degree of compaction is believed to be unacceptable for stacks used in commercial applications. Recent efforts to improve cathode compaction resistance emphasize heat treating and oxidation (1).

* Electrolyte loss: Long-term stability of cell and stack performance is, to a large extent, dependent on limiting electrolyte loss by corrosion and volatilization. Corrosion loss is largely limited to the first 2,000 h of operation. Loss by volatilization is a slow but continuing process. These two losses are considered to be manageable (excess electrolyte is stored or added), at least up to 10,000 h. Another problem is electrolyte leakage through the wet seal. This leakage occurs because the ambient oxygen which surrounds the cell is reduced to form carbonate ions on the outer surface of the cell (Fig. 3)
More carbonate ions are produced on the anode than on the cathode because the anode is at a lower potential. Some of the carbonate ions migrate and react at the anode. The remainder of the charge necessary for neutrality is transferred by the migration of alkali ions to the outer surface of the cell. The leaked electrolyte then migrates along the manifold gaskets to the top of the stack. Several engineering approaches to minimize electrolyte migration have been developed, and encouraging results have been obtained in subscale stack tests that operated over 5,000 h.

* Sulfur contamination: It is generally acknowledged that even ppm levels of sulfur may cause an unacceptable loss of cell voltage. Performance loss of a MCFC due to the presence of sulfur in the fuel and oxidant gases occurs primarily at the anode. The sensitivity of the nickel anode to hydrogen sulfide has been demonstrated in many studies and cell tests (13). The presence of sulfur dioxide in the oxidant (due to recycling of burned fuel to the cathode or in air) does not affect cathode polarization but affects anode performance, because sulfur dioxide in the oxidant will react to produce sulfate in the electrolyte and then be transported to the anode. In a cell, a concentration gradient of sulfate ions between cathode and anode is established, as hydrogen in the anode reduces sulfate to hydrogen sulfide. While there is a general agreement on the negative impact of hydrogen sulfide on fuel cell performance, the exact mechanism responsible for the performance loss is not clearly defined. Several possible mechanisms exist which may account for the decrease in cell performance: (a) Hydrogen sulfide can poison the hydrogen oxidation reaction by adsorbing on anode active sites and thereby blocking the desired molecules from adsorbing. (b) Adsorbed hydrogen sulfide can poison the water shift reaction, causing a hydrogen deficiency in the fuel cell, which in turn causes a drop in cell voltage (14). (c) Recently, it has been suggested that poisoning of the Ni anode is the result of electrochemical formation of a layer of nickel sulfide on the anode. The layer forms by reaction between the Ni electrode and dissolved sulfide ions in the electrolyte (15). Sulfur tolerant anode materials are being investigated.

* Internal reforming: It has been demonstrated that internal reforming in MCFCs is technically feasible (16). Internal reforming MCFCs can operate up to 5,000 h without performance decay. The performance of internal reforming cells is identical to that obtained with cells using simulated reformed fuels. However, the nickel reforming
catalyst used for internal reforming in MCFCs can be affected by one or another form of deactivation. To date, MgO-supported catalysts have demonstrated the best stability in the fuel cell (17). However, the catalyst slowly decays at longer times. The cause for the decay is physical blockage of catalyst active sites by the carbonate electrolyte. The electrolyte on the catalyst was found to be rich in potassium, indicating electrolyte transfer to the catalyst by vapor phase as well as creepage. Recent work on internal reforming emphasizes on developing a way to control electrolyte vapor transport and electrolyte creepage from the anode to the catalyst. It appears that finding a means to prevent both electrolyte vapor transport and electrolyte creepage for long periods of time is a major technical challenge.

IMPORTANCE OF ELECTROLYTE BASICITY IN MOLTEN CARBONATE FUEL CELLS

As discussed earlier, two of the critical issues in the development of MCFCs are cathode dissolution and bipolar plate corrosion. In cathode dissolution, the most important factor which determines the rate of NiO dissolution and transport (and, thus, the cathode lifetime) is the magnitude of the NiO solubility under fuel cell operating conditions. Therefore, knowledge of NiO solubility under various conditions is essential for evaluating NiO cathode endurance. In bipolar plate corrosion, accelerated corrosion of stainless steels in the anode gas atmosphere is due to oxide scale fluxing. The protective qualities of the scale is destroyed by the dissolution of the oxide in the carbonate electrolyte and precipitation of the oxide elsewhere as a non-protective porous mass. Thus, understanding the solubility of oxides in molten carbonates is important. In this respect, the electrolyte basicity plays an important role.

The solubility of an oxide depends on the basicity of the molten salt, and, in some cases, on oxygen partial pressure as well. The theory of the acid/base behavior of oxyanion salts is analogous to the Bronsted theory for aqueous solutions. In molten oxyanion salts, the oxide activity defines the basicity of the system. Thus, for a solvent such as Li2CO3-K2CO3 under a partial pressure of CO2, the basicity of the molten salt is given by the equilibrium

$$\text{CO}_3^{2-} = \text{O}^{2-} + \text{CO}_2 \quad [4]$$

The basicity of the melt may be altered by varying
the partial pressure of CO₂ and by varying the mole fraction of the components.

The dissolution of oxides in molten carbonates can be classified as basic and acidic. In basic dissolution, the solubility increases as the basicity increases. In acidic dissolution, the solubility decreases as the basicity increases. Plotting the logarithm of the concentration of a dissolved oxide in the molten salt (assuming an ideally dilute behavior corresponding to a concentration-independent activity coefficient) versus the basicity of the melt yields two straight lines, one corresponding to the acidic dissolution and one corresponding to the basic dissolution, and a minimum solubility is observed (Fig. 4).

In the case of NiO cathodes, for example, NiO is an amphoteric oxide and can dissolve as a base or as an acid (18,19). In a relatively acidic melt, NiO dissolves by dissociation

\[
\text{NiO} = \text{Ni}^{2+} + \text{O}^{2-} \quad [5]
\]

In a basic melt, NiO reacts with oxide to produce one of two forms of nickelate ions

\[
\text{NiO} + \text{O}^{2-} = \text{NiO}_2^{2-} \quad [6]
\]

or \[
2\text{NiO} + \text{O}^{2-} + \frac{1}{2}\text{O}_2 = 2\text{NiO}_2^- \quad [7]
\]

In the MCFC cathode environment, the melt is relatively acidic and the acidic dissolution is important.

For the acidic dissolution of NiO in molten carbonates, the solubility of the oxide decreases with increasing basicity of the melt. Therefore, making the MCFC cathode environment more basic is a means to lower the solubility of NiO and prolong the life of the NiO cathode. Basicity of the molten carbonate can be altered by (i) a change in the gas phase in equilibrium with the melt (e.g., lowering the partial pressure of CO₂ increases basicity), and (ii) a change in the carbonate melt composition (e.g., increasing the lithium content in Li₂CO₃-K₂CO₃ or adding basic oxides increases basicity).

The basicity of the molten carbonate can also play an important role in determining the properties of materials synthesized in the molten salt via its influence on the material stoichiometry. An example is the alternative cathode material LiFeO₂. The electronic resistivity of LiFeO₂ synthesized in carbonates was found to be dependent on the partial pressure of CO₂ above the
carbonate melt (thus the basicity of the melt). Synthesis with partial pressure of CO$_2$ < 0.005 atm produced LiFeO$_2$ with lower resistivity and the resistivity decreased with decreasing CO$_2$ partial pressure (20). This observation can be explained as follows. The partial pressure of CO$_2$ will affect the basicity of the carbonate melt (the activity of lithium oxide) and, in that way, can affect the cation ratio (Li/Fe) of the lithium iron oxide synthesized in the melt. Low partial pressure of CO$_2$ enhances the activity of lithium oxide, which tends to result in a more lithium-rich compound, i.e., a LiFeO$_2$ compound with a Li/Fe ratio > 1. Therefore, LiFeO$_2$ synthesized in more basic electrolyte is nonstoichiometric. As a result, a lower resistivity is observed.

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Fig. 1. Essential Components of a Molten Carbonate Fuel Cell Stack

Fig. 2. Subscale Stack Performance (2)
Fig. 3. Electrolyte Leakage through Wet Seal in a Bench-Scale Molten Carbonate Fuel Cell

Fig. 4. Solubility vs. Oxide Activity