THE ROLE OF MELT CHEMISTRY IN MOLTEN CARBONATE FUEL CELL [MCFC] TECHNOLOGY

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ABSTRACT
An overview is presented of recent developments in MCFC technology that are related to the melt chemistry. The status of chemical and electrochemical aspects of MCFC technology is reviewed, with emphasis on the electrode kinetics, in particular of the cathode, and on the corrosion mechanism of electrode and separator plate materials. Although the current demonstrations of large scale MCFCs all make use of Li-K carbonate eutectic, there is considerable interest in alternative electrolyte compositions. It appears that for the long-term performance of the MCFC, a Li-Na-K carbonate mixture with a composition close to that of the Li-Na eutectic would be advantageous.

Background: requirements for commercialization
This paper aims to give an overview and status report on some chemical and electrochemical issues that relate directly to the performance and stability of molten carbonate fuel cells. The molten carbonate fuel cell (MCFC), after intensive development during recent decades, is approaching commercialization. It is considered a prime candidate for efficient generation of electric power, and cogeneration of heat and power. In 1996 demonstrations of 250 kW-2 MW size MCFC plants will take place in the U.S. and Japan, while several European countries pursue MCFC development programs aimed at developing MW-size plants [1-3].

Cost issues determine the overall direction of current research related to MCFC technology. Whereas a few years ago, chemical and electrochemical questions dominated the research agenda, present emphasis is on new or improved materials, and on system design. However, chemical and electrochemical aspects of “performance” (power density) and “life time” (stability in long-term performance) remain of great importance.

Increasing the power density (presently 1.0-1.25 kW/m²) must be accomplished by improving electrode design and by pressurized operation (below 10 bar). Extending the life time of MCFC stacks (which now rarely exceeds 10,000 h), to at least 20,000 h in pressurized operation, requires a substantial reduction in performance decay [4]. Although much progress has been made recently, the performance decay of scaled-up cells and stacks (now in the range of 2-5 μV/h) is not completely understood and controllable. Further reduction by new materials and fabrication technologies must be based in insight in MCFC kinetics and corrosion.
Background: fundamental aspects

MCFC technology has almost from the beginning been based on the unique property of molten carbonates to remain invariant in contact with carbonaceous gas, and to be excellent ionic conductors in a temperature range starting at 600 °C, which is reasonably compatible with the operational range of natural gas reformers (optimally at 800 °C). Nevertheless, in spite of these unique properties, there are a number of fundamental difficulties connected with the application of molten carbonates in fuel cells.

1. First of all, the oxygen chemistry in these melts tends to be complicated by the presence of higher oxides (superoxide, peroxide, as well as unstable and adsorbed intermediates, see Table 1). This makes the oxygen reduction process relatively slow, compared, for example, to metal deposition from alkali chloride melts at the same temperature.

2. Furthermore, the capillary properties of molten carbonate are highly dependent on the gas atmosphere, as well as the type of substrate. Wetting angles can vary from close to zero for oxide type surfaces in melts under oxidant gas, to practically 60° at metals under reducing conditions. This exacerbates the “creeping” tendency of carbonates, which is well-known. Whereas creeping of molten salts is usually caused by a temperature gradient as driving force, in molten carbonates creeping is exacerbated by the combination with corrosion of metal surfaces and oxygen reduction at conducting oxide substrate. Nevertheless, in practice the creeping of molten carbonates can be controlled by careful design, in particular by avoiding steep concentration gradients in the gas composition and contact with corrodable materials. The latter, however, is difficult to accomplish, because of the third peculiarity of molten carbonates.

3. As is well-known, molten carbonates are extremely corrosive. This property is well understood in the case of metals, and the thermodynamics of the corrosion processes under various gas atmospheres have been known for some time. Only noble metals such as palladium and gold are resistant to corrosion by molten carbonate under and oxidant atmosphere. Even these noble metals dissolve slowly if the melt is strongly basic, for example in a Li-rich carbonate melt under very low CO₂ partial pressure. Nevertheless, certain alloys such as stainless steels are protected by a passive layer which retards (but does not eliminate) corrosion. However, the corrosion mechanism of alloys in molten carbonate is poorly understood.

Electrode kinetics: effect on power density

Target power densities of 2.0 to 2.5 kW/m² require increasing the current density from 1.65 to 3.0 kA/m² without lowering the present cell voltage (0.75 V). Table 2 shows approximate voltage-loss contributions for single cells at 1.65 kA/m². The ohmic (IR) contribution to overall voltage loss is not insignificant, but cannot be reduced
below a certain minimum level (typically that of a 1 mm thick electrolyte matrix), without causing gas cross-over. To further reduce IR-drop, recent work focuses on using as electrolyte the Li-Na carbonate eutectic, which has a 30% higher conductivity than Li-K eutectic, and also is less volatile [5,6].

It is not clear, however how this would affect the polarization of the cathode, which is the dominant voltage loss contribution. In the standard Li-K eutectic, polarization is due in equal measure to slow electrode kinetics, mass transfer resistance, and ionic-ohmic resistance of the cathode pores [7]. According to recently reported calculations, Li-Na carbonate eutectic would have a smaller cathode polarization than Li-K carbonate [5] (see Figure 1). This is confirmed by some experimental performance data [6]; however, other data are inconclusive, and appear to reinforce arguments that the lower oxygen solubility may limit the cathode performance in Li-Na mixtures (see Table 3).

Thus, there is a practical incentive to investigate the electrode kinetics of Li-Na and Li-Na-K mixtures more closely. It is desirable to review the traditional assumption that the oxygen reduction mechanism in such mixtures involves peroxide ions as primary reactants. Work by Reeves (see Figure 2) on electrode kinetics in Li-K mixtures containing Sr and Ca carbonate as additives [8] points to the inadequacy of existing mechanistic models, as does the discovery by Uchida and coworkers [9] of “spike peaks” presumably due to adsorbed intermediate products.

**Corrosion: effect on life time**

Recently, the corrosion of iron, nickel and chromium, and various alloys (especially Types 310 and 316 stainless steel) has been investigated systematically [10]. The role of surface layers of LiFeO₂, which conducts well but is porous, and of LiCrO₂, which is compact and dense, is becoming increasingly clear (see in this volume, Yazici and Selman, and Yanagida et.al.). But the detailed mechanism (kinetics and diffusion) by which these corrosion layers form, and a quantitative correlation with the corrosion rate, in short term and long term operation, still escapes us.

Combining optical observation with electrochemical in-situ techniques and post-test analysis can yield new insights. Recent work at IIT [11,12] has revealed the surprisingly dynamic and non-uniform character of the oxidation of metals such as nickel, which takes place during in-situ oxidation of nickel metal to form a NiO cathode. Figure 3 shows various stages of the oxidation process, which is accompanied by gas evolution.

It appears that also from the viewpoint of NiO dissolution and metal corrosion as a factor in cell life, Li-Na carbonate has advantages (Table 3, Figure 4).
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Table 1. Possible oxygen reduction mechanisms

Superoxide Path

\[ 3O_2 + 2CO_3^{2-} \rightarrow 4O_2^2 + 2CO_2 \]

\[ O_2^2 + e^- \rightarrow O_2^{2-} \quad \text{RDS} \]

\[ O_2^{2-} + CO_2 + e^- \rightarrow [O^-] + CO_3^{2-} \]

\[ [O^-] + e^- \rightarrow O_2^{2-} \]

\[ O_2^{2-} + CO_2 \rightarrow CO_3^{2-} \]

\[ i_o \propto O_2^{0.625}CO_2^{-0.75} \]

Peroxide Path

\[ O_2 + 2CO_3^{2-} \rightarrow 2O_2^2 + 2CO_2 \]

\[ O_2^2 + CO_2 + e^- \rightarrow [O^-] + CO_3^{2-} \quad \text{RDS} \]

\[ [O^-] + e^- \rightarrow O_2^{2-} \]

\[ O_2^{2-} + CO_2 \rightarrow CO_3^{2-} \]

\[ i_o \propto O_2^{0.75}CO_2^{-1.25} \]

Percarbonate Path

\[ O_2 + 2CO_3^{2-} \rightarrow 2CO_3^{2-} \]

\[ CO_3^{2-} + e^- \rightarrow [O^-] + CO_3^{2-} \quad \text{RDS} \]

\[ [O^-] + CO_2 + e^- \rightarrow CO_3^{2-} \]

\[ i_o \propto O_2^{0.75}CO_2^{-0.25} \]

Table 2. Approximate contributions to voltage loss (in mV) of single MCFC cells operating at 1.65 kA/m², 1 bar, 923 K (ref. 1,4)

|                  | State of the art | Future improved design |
|------------------|------------------|------------------------|
| Cathode          | 120-80           | 60-55                  |
| Anode            | 60-10            | 50-10                  |
| Electrolyte matrix| 50-55            | 25-40                  |
| "Nernst Loss"    | 65-145           | 65-145                 |
| Total            | 295-290          | 200-250                |

Note: Polarization and Nernst loss depend on specifics of gas composition and utilization.
Table 3. Physical properties of molten carbonates at 650 °C

|                       | Li₂CO₃/K₂CO₃(62/38) | Li₂CO₃/Na₂CO₃(53/47) |
|-----------------------|---------------------|----------------------|
| O₂ solubility (mol/cm³·atm) | 3.3x10⁻⁷      | 1.8x10⁻⁷           |
| Basicity (pO⁻²)       | 6.9                | 6.62                |
| Electrical conductivity (Ω⁻¹·cm⁻¹) | 1.4~1.6       | 2.1~2.3             |
| Electrolyte vapor loss (g cm⁻³) | -32x10⁻¹⁰   | -3.5x10⁻¹⁰         |

References:
- Advances in Molten Salt Chemistry Vol. 4
- Physical Properties Data Compilations Relevant to Energy Storage

Figure 1. Cell voltage vs. operation pressure with different electrolyte mixtures (ref. 5)
Figure 2. Effect of SrCO₃ on the Steady State Performance in Li/K(50/50) carbonate. $P_{O_2}=0.33$, $P_{CO_2}=0.67$, $T=650 \, ^°C$. (ref. 8)
Figure 3. Time development of nickel oxidation under gas evolution in carbonate melt at 650 °C (ref. 11)

Figure 4. Solubility of NiO in various melts as a function of $P_{CO_2}$ at 1023 K (Ota et al., JES, Vol. 139, No. 3 (1992))