MOLTEN CARBONATE FUEL CELLS

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Summary

Molten carbonate fuel cells use carbonate salts of alkali metals as electrolyte. Due to the highly corrosive nature of the electrolyte, various countermeasures are being developed. MCFCs are expected for high-efficiency power generation systems using hydrocarbon fuels, such as natural gas and coal gas. This article describes the mechanisms of operation and cell degradation, as well as the features of MCFC systems.

1. Introduction

MCFCs, or molten carbonate fuel cells, use carbonate salts of alkali metals as electrolyte. The cell operating temperature is high at 650 °C (923 K); in this kind of environment, relatively cheap nickel can be used as the catalyst instead of a precious metal such as platinum. In addition, the use of nickel enables the use of reformed gas from hydrocarbon fuels such as coal gasification gas containing a large amount of carbon monoxide. This diverse range of fuels is an important merit of MCFCs in addition to the possibility of high efficiency expected for combined cycle systems.

2. Principle of Operation and Construction of MCFCs

The basic configuration of MCFCs appears in Figure 1. An MCFC consists of an ion-conducting electrolyte matrix, two electron-conducting electrodes, and an electron
conducting separator plate reactant gas flow channels. The electrode reactions for MCFCs are as follows.

Cathode: $2\text{CO}_2 + \text{O}_2 + 4e^- \rightarrow 2\text{CO}_3^{2-}$

Anode: $2\text{H}_2 + 2\text{CO}_3^{2-} \rightarrow 2\text{H}_2\text{O} + 2\text{CO}_2 + 4e^-$

Overall reaction: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$

As can be seen here, the overall reaction is a water producing reaction between oxygen and hydrogen, with the carbonate ions $\text{CO}_3^{2-}$ acting as intermediate agent to transfer oxide ion from cathode to anode. Electrons produced at the anode pass through an external circuit before flowing to the cathode, and thus electric power can be extracted.

The alkali metal carbonates are used as the electrolyte in MCFCs. These carbonates are solid at room temperature, but they exhibit ion conductivity in a molten state at elevated temperatures and thus can be used as the electrolyte. Because of the high conductivity of molten carbonates, there is no need for a supporting electrolyte like those needed when using water or organic solvents as electrolytes.

In actual fuel cells, the melting point of a single carbonate salt is high, and so a binary eutectic salt is used; generally $\text{Li}/\text{K} = 62/38$ mol% (melting point 488 °C) or $\text{Li}/\text{Na} = 53/47$ mol% (melting point 496 °C). The fuel cell is actually operated at a temperature of 650 °C or so in consideration of the carbonate conductivity, gas solubility, and other factors. Because this molten carbonate material is extremely corrosive, lithium aluminate ($\text{LiAlO}_2$) or some other ceramic material is used to contain the electrolyte.

For this electrolyte support material, fine ceramic powder is used as the principal component in a mixture with large-size ceramic powder and ceramic fibers which reinforce the mechanical strength. Generally, these ceramic components and a polymer material called a binder are used to create slurry, which is then formed to a sheet with a constant thickness. After lining the inside of the fuel cell with this sheet, it is thermally treated in order to eliminate the organic components, and it is baked.

The sheet is then impregnated with the carbonate electrolyte so that it functions as an electrolyte matrix. The electrochemical reaction occurs at porous gas diffusion electrodes, in which gas diffuses easily while keeping sufficiently large areas of reaction sites. Nickel oxide is used as cathode catalyst. It has low electron conductivity, but by doping the nickel oxide crystal lattice with lithium in the carbonate, the electrode provides good electron conductivity.

For the anode, nickel metal is used as electrode catalyst. In actuality, a nickel alloy containing several percent chromium or aluminum is used in order to suppress creep in the porous electrode.

Metal materials can be used in the separator and current collector. However, in addition to the corrosive properties of the carbonate, these materials are also exposed to both oxidizing and reducing atmospheres, and so must satisfy strict requirements in order to
prevent each material from being damaged. In the reducing atmosphere, a nickel-base alloy is used; in the oxidizing atmosphere, stainless steel; SUS310S, SUS316L; is used. Also, a wet seal is employed on the outer periphery of the separator to prevent leakage of fuel gas and oxidizer gas outside the cell. This gas sealing function can be obtained by causing molten carbonate to permeate the surface of contact between the electrolyte matrix and the separator. Since this is also the area in which the separator makes direct contact with the carbonate, countermeasures need to be prepared. In such an atmosphere as considered here, it is difficult to form a metal oxide film on the surface of stainless steel, which is resistant to oxidation. Therefore, the surface of the wet seal area is covered with alumina (Al₂O₃) or lithium aluminate (LiAlO₂) by means of aluminized coating to endow it with corrosion resistance.

Figure 1. Schematic Illustration of an MCFC Unit Cell

At the operating temperature of ~650 °C (923 K) for MCFCs, the fuel cell reactions proceed vigorously, and the nickel of the electrodes also acts as a catalyst. On the anode side, the nickel serves as a catalyst causing carbon monoxide to react with steam, producing hydrogen and carbon dioxide gas. In other words, carbon monoxide can also be used in MCFCs as a fuel, according to the shift reaction described as:

\[ CO + H₂O \rightarrow H₂ + CO₂ \]

MCFCs can utilize the coal gasification gas. It is produced from coal in a coal gasifier, and is mainly composed of carbon monoxide and hydrogen. As for natural gas, the steam reforming method is necessary to convert it into a hydrogen enriched gas mixture, which can be used as fuel for a fuel cell.

Depending on where the reformer is placed, MCFCs can be classified into external and internal reforming types; in particular, the latter type integrates a reformer within a cell stack so that the cell generated heat can be efficiently utilized as heat of the reaction for fuel reforming. (see Table 1.) Fuel reforming catalyst layers are situated on the anode side.
Table 1. Comparison of Reforming Methods for MCFC Systems

<table>
<thead>
<tr>
<th>Refiner aspect</th>
<th>External reforming type</th>
<th>Internal reforming type</th>
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</thead>
<tbody>
<tr>
<td>Construction</td>
<td></td>
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<tr>
<td>Feature</td>
<td></td>
<td>* Higher efficiency compared with external reforming type but complex fuel cell construction not suited to large-scale systems</td>
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<tr>
<td></td>
<td>* Stack maximum power output 1 to 2 MW</td>
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</tbody>
</table>

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crystal phase of lithium aluminate as a function of temperature, partial pressure of CO₂, and initial grain diameter.

Biographical Sketch

Kouichi Takizawa was born 8 January 1964, in Japan. He is a researcher in fuel cell technology, and has a Master of Engineering in electrochemistry from Tohoku University. He joined TEPCO in 1988.