Longer Lasting and More Efficient Molten Carbonate Fuel Cells due to Improvements in Ceramic Materials and their Production Process

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ABSTRACT

Emergy indicators of the industrial production and pilot-plant operation of Molten Carbonate Fuel Cells (MCFC) are presented, as a continuation of ongoing research on Hydrogen-based technologies. MCFCs are very likely to shortly reach the commercialization phase, as a result of the recent intense efforts in the development of innovative ceramic components (anode, cathode and matrix), as well as metallic components, which are now characterized by higher corrosion resistance and more constant performance in time. These kind of fuel cells are being developed by the National Agency for Energy and Environment (ENEA, Italy), in collaboration with several Italian enterprises (e.g., Ansaldo Fuel Cells Srl, Venezia Tecnologie, FN SpA) under an R&D activity funded by the Italian Government. The present analysis is based on process data directly provided by the partners.

This analysis provides a special insight into the improvements in the final energy and environmental performance of the cells, made possible by means of innovative materials also aimed at extending the fuel cell lifetime. It was also possible to highlight the process steps requiring the largest emery input and to identify the specific items that contribute to a larger extent to the total emery cost. Performance and loading indicators were also calculated and compared for several independent improvement options over different lifetime scenarios and compared with other power plant technologies.

INTRODUCTION

Molten Carbonate Fuel Cells (MCFC) are currently on the cutting edge of research on electrochemical devices for stationary applications. Similar to batteries, they convert chemical energy of the feedstock chemicals into electric energy. MCFCs can directly use pure hydrogen, hydrogen-rich gases, natural gas, or even gasoline for fuel. This fuel flexibility gives them a significant advantage over other electricity generation alternatives (e.g., thermal generation) since hydrogen fuel can be produced either from conventional fossil fuel sources and/or renewable/alternative sources, such as landfill gas. The fuel flexibility is possible thanks to the MCFC’s resistance to fuel impurities such as sulfur and particulates. Moreover, they are not sensitive to carbon monoxide or carbon dioxide "poisoning," instead they can even use carbon oxides as fuel. In addition, non-precious metals can be used as catalysts at the anode and cathode, thus reducing production costs.

Other advantages are high fuel-to-electricity conversion efficiency (approaching 60% efficiency in hybrid configuration), modularity, low emissions, and low noise. These two latter characteristics can be highly relevant in urban areas where air quality and noise are frequent problems. Disadvantages at the current stage of development are mainly low duration time (compared to other more mature power plant technologies), high production costs, and, consequently, low market
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The durability issue is mainly due to the corrosive electrolyte used, which accelerates component breakdown and corrosion.

Worldwide there are already many demonstration units based on fuel cell technology (http://www.fuelcells.org/info/charts/FCInstallationChart.pdf) and there are also many projects for introduction into the market. In particular, the present paper is an outcome of the five year (and still ongoing) collaboration between the Department of Chemistry of the University of Siena, ENEA (Italian National Agency for New Technologies Energy and the Environment), and Ansaldo Fuel Cells SpA for the complete Life Cycle Assessment (LCA) of Molten Carbonate Fuel Cells (MCFCs). MCFCs are a particular kind of high temperature fuel cell designed for stationary use in urban areas and are under development by ENEA, in collaboration with several Italian enterprises (e.g., Ansaldo Fuel Cells Srl, Venezia Tecnologie, FN SpA) under an R&D activity funded by the Italian Government.

The first part of the collaboration included Life Cycle Assessment (LCA) combined with emergy efficiency indices for the environmental impact evaluation stage of LCA (Ulgiati et al., 2006). Hydrogen fuel production via different technologies, such as natural gas steam reforming, coal gasification, water electrolysis from fossil energy sources, and hydropower was analysed (Bargigli et al., 2004a). During the course of the work, LCA of the main materials used for fuel cells components, (i.e., nickel, chromium [Tabacco et al., 2002], aluminium [Bargigli, 2004c], and steel [Bargigli and Ulgiati, 2003]) and fuel for the FC operating phase (i.e., natural gas and coal) were performed. Subsequently, a comprehensive evaluation of a previously designed 500 kW MCFC pilot plant was made and compared to other more conventional natural gas fuelled power plants (Raugei et al., 2003a and 2005). This evaluation revealed that the MCFC plant showed very promising environmental performance even in comparison with other more mature and widespread technologies.

Current research on MCFC is now focusing on stabilizing the performance of the fuel cells and enhancing their duration time by changing/adjusting the composition of the fuel cell components and by increasing their corrosion resistance. Different improvement options are subject to environmental impact assessment by our research group. In this paper the emergy efficiency indices of the original stack, which was active only for 20,000 hours compared to the target of 40,000 hours, are presented. They are then compared to the new alternatives to investigate the most advantageous improvement option. Disaggregated values are not presented because of confidentiality agreements. For more detailed information please refer to our full report (Ulgiati et al., Report to ENEA, 2005, in Italian).

THE EVALUATION METHOD

The applied method, called SUMMA (Sustainability Multiscale Multimethod Assessment), was developed by our research group in the last few years (Ulgiati et al., 2006) and it is still being refined. SUMMA is a Life Cycle Assessment method in accordance with the ISO and SETAC standards (ISO 14040:1997; ISO 14041:1998; ISO 14042:2000; ISO 14043:2000; SETAC 1993). The environmental impact assessment stage of SUMMA (compare to the third step of the LCA) includes Material Flow Accounting (Schmidt-Bleek, 1998; Ritthof et al., 2002; Bargigli et al., 2004a), Embodied Energy Analysis (Herendeen, 1998), and Emergy Synthesis (Odum, 1996; Brown and Ulgiati, 2004). These assessments deal with upstream impacts of resource depletion, sustainable use of resources, and renewability. For downstream impacts the CML 2 baseline 2000 method (CML, 2000) is used resulting in various impact categories, such as toxicity. Finally, sensitivity analysis is used to counter-check the results and highlight potential pivotal contributions among the input flows. In this paper only the results of the emergy evaluation are presented and discussed. All the data for the mass flow inventory, where available, were provided directly by the producers and, therefore, are to be considered highly reliable.
CASE STUDY

The “First of a Kind” Stack

The main fuel cell components are anode, cathode, matrix, electrolyte, and special steel parts. Each component is subject to a different production chain, different chemical inputs, and materials, all of which were studied with the LCA method. After the fuel cell components are produced, the stack is assembled and enters the start up phase. After that, the operation phase follows, where natural gas is used as feedstock to the fuel cell system. The system includes an external natural gas steam reformer for hydrogen fuel production, thermally integrated in the fuel cell system. The “first of a kind” MCFC stack shut down early (20,000 hours reference time). In fact, it is not yet expected that present stack technology is able to reach the target operation lifetime of 40,000 hours. The need for material improvements thus arose, together with the need for a comprehensive environmental impact assessment.

Improvement Options

One of the first changes that were made in the MCFC project involved the fuel cell design and optimization of fuel use. The new version of the MCFC prototype included lower use of natural gas and water feedstock and a more efficient heat balance of the system. Further research on MCFC components has then focused on improvement options regarding both composition and manufacturing of fuel cell components. For example, a new anode composition is now being tested, which would allow the use of the less environmentally harmful Al-Ni alloy, compared to using Ni-Cr alloy as active substance. At the same time, the manufacturing process has changed in order to better control the porosity of the metal powders. This is expected to result in more constant performance and higher corrosion resistance for the anode. Similar improvements have been made to the matrix and the electrolyte as well.

While the optimization of the anode, matrix, and electrolyte are at a good stage of development and can be considered already fixed, there are still three possible routes for cathode optimization. Consequently, improvements regarding all the components except the cathode (i.e., electrolyte, matrix, and anode) are referred to collectively as New Asset (= new components excl. cathode changes), and compared to the original version, called Old Asset.

The first studied case is called Cathode Option I and consists of the New Asset with a new cathode composition and a slightly different production process, mostly based on nickel, magnesia, and iron oxides instead of the use of nickel only. The second case, called Cathode Option II, consists of the New Asset with a capture layer of lithium and iron oxides between the nickel cathode and the matrix. The third case, Cathode Option III, includes dipping the cathode into a cobalt salt solution in order to prolong the life of the cathode.

RESULTS AND DISCUSSION

Table 1 presents transformities of electricity produced with MCFC and other technologies that are based both on the use of fossil fuels (oil and natural gas) and renewable energy sources (hydropower, wind power, and advanced photovoltaic). The comparison highlights that even at their early stage of development, MCFCs are able to compete, in terms of energy efficiency, with the more mature and developed technologies using oil for fuel. The improvements of the MCFC operation phase recently performed by Ansaldo have already increased the efficiency as measured by reduced transformity, which was mainly caused by the reduction of natural gas feedstock (case MCFC5 in Table 1). It is highly probable that, as MCFC technology matures in the future, it will also be
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competitive with natural gas power plants. MCFCs also have the additional advantage of being modular and, therefore, may be used within urban areas and small-size private installations.

The percentage breakdowns of the total emergy requirement (TER, synonymous to emergy yield) in all the considered options are presented in Table 2. First of all, it is important to underline that the various technological options and innovations, even if they are crucial to reach the target lifetime of 40,000 hours, in general, had little impact on the emergy indices addressed. Instead, these indices are largely determined by the amount of natural gas used. This is the most apparent result of the analysis.

It is also noteworthy that among the three cathode options there are no significant differences in terms of emergy. Only the second cathode production process (Option II) seems to show a slightly higher contribution to the TER, which is its self slightly higher in absolute terms.

We see four possible causes for that fact that almost no difference in emergy efficiency derived from material improvements of MCFC was detected: 1) there are no significant differences, 2) the technical differences between the analyzed cases are too small to be detected by the emergy indices

Table 1. Transformities1 of electricity from different technologies.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Oil plant2</th>
<th>NG plant3</th>
<th>MCFC4</th>
<th>MCFC5</th>
<th>Hydro7</th>
<th>Wind8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transformity (seJ/J) (excl. services)</td>
<td>3.31x10^5</td>
<td>1.53x10^5</td>
<td>2.54x10^5</td>
<td>2.18x10^5</td>
<td>1.02x10^5</td>
<td>1.06x10^5</td>
</tr>
</tbody>
</table>

1The new baseline of 15.83x10^24 sej/year (Odum, 2000 was used. Since MCFC (Molten Carbonate Fuel Cell) are still in the pre-commercialization phase, the services would be overestimated if included in the accounting.
2Source: Table IX in Brown and Ulgiati (2004).
3Updated value from Raugei et al. (2003a), according to the new emergy baseline. NG=natural gas.
4Updated value from Raugei et al. (2003a), according to the new emergy baseline and referring to the Old Asset (old stack components and design) with a target value of 20,000 hours of operation lifetime.
5Updated value according to the new emergy baseline and referring to the New Asset with a target value of 40,000 hours of operation lifetime.

Table 2. Emergy indices1 of improvement options of Molten Carbonate Fuel Cells.

<table>
<thead>
<tr>
<th>Emergy indices</th>
<th>Old Asset3</th>
<th>Old Asset4</th>
<th>New Asset5</th>
<th>New Asset Option I6</th>
<th>New Asset Option II7</th>
<th>New Asset Option III8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Emergy Requirement (TER)</td>
<td>4.35x10^18</td>
<td>8.10x10^18</td>
<td>7.48x10^18</td>
<td>7.48x10^18</td>
<td>7.53x10^18</td>
<td>7.48x10^18</td>
</tr>
<tr>
<td>TER % for stack production only</td>
<td>9.3%</td>
<td>5.0%</td>
<td>5.25%</td>
<td>5.27%</td>
<td>5.74%</td>
<td>5.23%</td>
</tr>
<tr>
<td>TER % for stack operation only</td>
<td>87.1%</td>
<td>93.1%</td>
<td>92.74%</td>
<td>92.73%</td>
<td>92.07%</td>
<td>92.77%</td>
</tr>
<tr>
<td>TER % for direct labor only</td>
<td>3.6%</td>
<td>1.9%</td>
<td>2.00%</td>
<td>2.00%</td>
<td>2.19%</td>
<td>2.00%</td>
</tr>
<tr>
<td>Energy cost for stack production (sej/kW)</td>
<td>8.11x10^14</td>
<td>8.11x10^14</td>
<td>7.86x10^14</td>
<td>7.88x10^14</td>
<td>8.65x10^14</td>
<td>7.82x10^14</td>
</tr>
<tr>
<td>Transformity of electricity (seJ/J)</td>
<td>2.54x10^5</td>
<td>2.36x10^5</td>
<td>2.18x10^5</td>
<td>2.18x10^5</td>
<td>2.20x10^5</td>
<td>2.18x10^5</td>
</tr>
</tbody>
</table>

1excluding services and indirect labor. Because Molten Carbonate Fuel Cells (MCFC) are still in the pre-commercialization phase the services would be overestimated if included in the accounting. The new baseline of 15.83x10^24 sej/year [Odum, H.T. 2000] was used.  
2 = data refer to the 500 kW, MCFC stack and are expressed in sej per kWe generated  
3Old Asset = old stack components and design. 20,000 hours operation time.  
4Old Asset = old stack components and design. 40,000 hours operation time.  
5New Asset = new design, new electrolyte, new matrix and new anode but old cathode. 40,000 hrs operation time.  
6Option I = New Asset and new cathode with Ni, Fe, and Mg oxides. 40,000 hours operation time.  
7Option II = New Asset and new cathode with capture layer of Li and Fe oxides. 40,000 hours operation time.  
8Option III = New Asset and new cathode covered with Li and Co oxides. 40,000 hours operation time.
available, or 3) transformities of minerals and chemicals are very crude (e.g., transformities of minerals are often all set equal to $1.68 \times 10^9$ sej/g due to a lack of more precise data), and 4) the method is an intrinsically donor-side method based on global flows of energy and nature does not differentiate much between the nickel and chromium earth cycles, thus there should be little difference detected. Having access to more precise transformities for different elements would improve the precision in the energy assessment and enhance the chances of finding differences between the material improvement options of this present study. The recent efforts to estimate detailed transformities for minerals by Cohen et al. (this proceedings) and Martinez et al. (this proceedings) is thus of invaluable importance for emergy analysts.

Figure 1 highlights the great impact on transformities when comparing options involving the use of different feedstock fuels. This comparison includes the possible final transformities of electricity from MCFC, considering different fuel sources and energy conversion technologies for the production of hydrogen fuel. The fuel cell system under study (MCFC + integrated steam reformer) is compared to the results from a previous paper by Bargigli et al. (2004a) on different hydrogen production routes. In that paper the analyzed systems were hydrogen from centralized natural gas steam reforming, coal gasification, and alkaline water electrolysis using electricity from both fossil fuels (natural gas and diesel) and renewables (hydropower).

It is apparent that the by far poorest result (higher transformity) is shown by the water electrolysis technology using electricity generated from fossil fuels. This is caused by the additional and low-efficiency energy conversion step needed to produce electricity from natural gas or diesel oil combustion. Once it is generated, electricity from fossil fuels is then used for hydrogen production in the electrolytic cell with quite high energy efficiency (around 80%). For water electrolysis technology, a much better result (lower transformity) is found in the case of electricity generated from the use of hydropower. Raw syngas production from coal gasification shows the lowest electricity transformities due to the lower transformity of coal fuel than the one of natural gas.

![Figure 1. Transformities of electricity from Molten Carbonate Fuel Cells (MCFC) using different energy sources for hydrogen production. (The new global emergy baseline of 15.83 x 10^24 sej/year [Odum, 2000] was used.)](image-url)
Natural gas steam reforming technology, both in the cases of centralized (dedicated large scale plants) and on site production (local small scale steam reformer coupled with MCFC stack), still shows good performance.

CONCLUSIONS

The analysis has shown that although Molten Carbonate Fuel Cells are still at an early developmental stage, they are competitive with oil-fired power plants and show promising performance also in respect to natural gas-fired power plants. Furthermore, the analyzed technological innovation options do not affect emergy efficiency significantly, which is instead largely dominated by the use of natural gas in the fuel cell system. This provides a useful indication that changes in the fuel cell components, which are made in order to extend the fuel cell duration, do not significantly influence the overall resource efficiency as measured by emergy synthesis. However, this could also indicate that emergy databases still need to be extended and refined compared to other life cycle impact assessment methods, which already benefit from more developed and detailed databases. That said, emergy efficiency indices can provide useful information when comparing different options involving different fuel sources in studies of technological development similar to this present one.

REFERENCES


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