Investigation on a ionic liquid matrix for decreasing MCFC working temperature

F. Rossi¹, R. Germani², A. Nicolini¹, P. Di Profio²

¹University of Perugia, Department of Industrial Engineering, Perugia, Italy
²Center of Excellence on Innovative Nanostructured Materials, University of Perugia, Perugia, Italy

Introduction
Molten Carbonate Fuel Cells (MCFCs) are characterized by high working temperatures (600-700°C). They have high efficiencies. The primary problem of MCFCs is durability; high temperatures and the typical used electrolyte accelerate the cell components breakdown and corrosion; thus, the cell life may be not satisfactory for stationary use. An original patented small size MCFC was proposed and tested in previous works [1-4]. The proposed cylindrical geometry allowed to obtain benefits with respect to the traditional MCFCs in terms of construction time and costs, thermal dispersion minimization, global efficiency; minimization of gases tight problems, compression strain uniformity on the contact surface. The present paper regards an investigation on using ionic liquids as electrolyte support in the aforesaid MCFC instead of a lithium aluminate porous element. In the traditional cylindrical MCFC, carbonate liquefaction is needed in the carbonates-glycerine mixture starting at 500°C. This phase may be avoided by using ionic liquids, which are low melting point (<100°C), thermally stable (up to 200°C) salts which represent a new class of non-molecular, ionic solvents. They are able to solvate a broad spectrum of both organic and inorganic compounds, have low vapour pressure, are recyclable and easily handled [5-6]. Thus, ionic liquids may help the charge separation at temperatures lower than 150-200°C. They may support the carbonate ion production and passage through the matrix; thus, they may be suitable as matrix support. The advantage is to reduce the MCFC working temperature; thus, a low temperature MCFC (LTMCFC) may be obtained. The LTMCFC life may be significantly longer than a traditional MCFC one. A single LTMCFC experimental facility was built and used for preliminary tests. Different kinds of ionic liquids were tested. Electrolytic solutions were made by ionic liquids (solvent) and lithium-potassium carbonates (solute). Tests were led at temperatures lower than 200°C in order to verify the proposed solution at temperatures very low with respect to traditional MCFC ones. Tests were made by supplying the proposed facility with hydrogen. The produced voltage and current were evaluated for each kind of ionic liquid matrix by varying the applied load and temperature. Preliminary tests allowed to verify the suitability of the proposed solution and may be useful to individuate possible other adjustment for performances improving.

Synthesis of Ionic Liquids (ILs)
One of the very interesting aspects of ILs is the possibility to alter their physical and chemical properties by varying their structure, with respect to the choice of organic cations and anions, and side-chain attached to the organic cation; thus, ILs have been described as 'designer solvents' [5-6]. The ILs used in this study were 1-octyl-3-methylimidazolium hexafluorophosphate (OMIM PF6, IL1) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM BF4, IL2). IL1 and IL2 were synthesized starting from 1-methylimidazole and the appropriate alkyl halide (alkyl = octyl for IL1 and butyl for IL2), and then by subjecting the obtained imidazolium chlorides to anion exchange with hexafluorophosphoric acid (IL1) or fluoroboric acid (IL2).

The experimental reactor
An experimental reactor was designed and built to test the new ionic liquid matrices; it has a cylindrical shape. It is made by the following polytetrafluoroethylene (PTFE) components:
1) LTMCFC compartment: it is the central compartment (see Figure 1 and 2a). The ionic liquid - carbonates electrolyte is installed here between the electrodes (the nickel-chrome porous anode and the nickel oxide cathode). A metallic net is installed on each electrode external side for voltage-current measurement and as electrode support system. Anode, cathode and metallic
nets are supported by a holed PTFE wall in the supplied gases side. The holed PTFE wall allows the gas tight and supplying.

2) Anodic gases compartment (see Figure 1): it is connected to the anodic gases distribution system by copper pipes in the lateral side. Hydrogen and nitrogen are supplied to the anode by the holed PTFE wall;

3) Cathodic gases compartment (see Figure 1): it is connected to the cathodic gases distribution system by copper pipes in the lateral side. Air, carbonic dioxide and nitrogen are supplied to the cathode by the holed PTFE wall.

4) a plug which closes the reactor. The plug is characterized by (see Figure 2b):
   - anodic and cathodic outlets over the electrode compartments;
   - a central hole for the installation of a thermocouple for electrolyte temperature measurements;
   - four holes (two for each electrode net) for voltage and current measurements by copper leads;
   - a plugged hole for electrolyte solution restoring over the electrolyte compartment;
   - two groovings in the plug bottom side for electrodes and metallic nets casing.

Figure 1 – the experimental reactor (upside view)

Figure 2 – (a) the experimental reactor (perspective view); b) the reactor plug
A pressurization system allows keeping the gases compartments at a pressure 50mbar higher than the LTMCFC one; this adjustment increases the electrolyte solution tight. The experimental facility is made by the reactor, a gas supplying system and a heating system. The heating system is made by a thermostatic bath constituted by silicon oil in a steel box. An electromagnetic agitator and heater allows the bath uniform heating. Besides, the facility was thermally insulated during the tests in order to minimize the thermal dispersions. The facility is shown in Figure 3.

The experimental tests
Experimental tests were made by the facility with different electrolyte solutions constituted by ionic liquids and carbonates. Two kinds of ionic liquids were tested (identified by IL1 and IL2 codes). Their characteristics in terms of kinematic viscosity (measured by Ubbelohde viscosimeters soaked into thermostatic baths) and electrical conductivity (measured by a conductivimeter) are shown in Table 1. The tested electrolyte solutions were made by the ionic liquids (solvent) and carbonates (solute) 5% or 9.7% by weight. It was verified that carbonates mixing does not modify the electrical conductivity of the ionic liquids.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Kinematic viscosity at 25°C (m²/s)</th>
<th>Electrical conductivity at 25°C (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL1</td>
<td>3.46*10⁻⁴</td>
<td>0.02</td>
</tr>
<tr>
<td>IL2</td>
<td>3.87*10⁻⁵</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Tests were made for three LTMCFC temperatures: 50, 100 and 150 °C. Open-circuit voltages were measured and electrical loads were applied to measure the electrical current on a closed circuit. For brevity, Table 2 reports only open-circuit voltages, 1.5 ohm load voltages and 1.5 ohm load currents. Results shows that only IL1 allows the LTMCFC working. IL2 application does not
produce voltage and obviously current. Gas chromatographic analyses were made on inlet and outlet gases relatively to IL1 tests; results verified that the reaction occurs correctly both for cathodic and anodic compartment.

Table 2: experimental tests results (IL1-based electrolyte)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Temperature (°C)</th>
<th>Open-circuit voltage (V)</th>
<th>Voltage produced when a 1.5 ohm load is applied (V)</th>
<th>Current produced when a 1.5 ohm load is applied (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL1+carbonates solution</td>
<td>50</td>
<td>0.062</td>
<td>0.010</td>
<td>0.030</td>
</tr>
<tr>
<td>(carbonate 5% by weight)</td>
<td>100</td>
<td>0.037</td>
<td>0.010</td>
<td>0.042</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.032</td>
<td>0.020</td>
<td>0.060</td>
</tr>
<tr>
<td>IL1+carbonates solution</td>
<td>50</td>
<td>0.068</td>
<td>0.010</td>
<td>0.021</td>
</tr>
<tr>
<td>(carbonate 9.7% by weight)</td>
<td>100</td>
<td>0.038</td>
<td>0.013</td>
<td>0.041</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.034</td>
<td>0.022</td>
<td>0.351</td>
</tr>
</tbody>
</table>

In particular, IL1-carbonates solution works as good electrolyte when the carbonate percentage is about 10% by weight at 150°C. Otherwise, very low current is measured (also for different applied electrical load) for lower temperatures or lower carbonates percentage. Thus, the reported preliminary tests allows to define the proposed matrix as possible solution for decreasing MCFC working temperature.

Conclusions

Preliminary experimental tests were carried out to verify the suitability of the proposed ionic liquid-based new matrix for cylindrical MCFCs. An experimental facility was built constituted by a reactor, a heating system and a gas distribution system. Two kinds of ionic liquids were tested as support for matrix realization. Tests were carried out for temperatures up to 150°C. Results showed that IL1 ionic liquid may be a good solution for decreasing MCFC temperature and increasing MCFC life. Investigations are going on to individuate solutions and adjustments for testing the proposed matrix on the cylindrical single MCFC or stack [1-4]. The optimized solution may help to build low temperature MCFC (LTMCFC) limiting components corrosion and breakdown problems.

References