Carbon–air fuel cell development to satisfy our energy demands

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Received: 15 December 2006 / Accepted: 2 April 2007 / Published online: 24 October 2007
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Abstract Carbon is an exceptionally versatile fuel source, with excellent conductivity properties and an extraordinarily high energy density. This paper describes the evolution of carbon–air fuel cells to produce electrical energy, the use of renewable carbon in carbon-neutral processes and greenhouse gas reduction and the long-term future of such cells.

Keywords Renewable energy · Direct carbon fuel cells

Historical background

There is an enormous global demand for portable high energy density power sources. In an era dominated by environmental and climate change concerns (the global average atmospheric CO₂ concentration increased from 280 ppmv in 1800 to 380 ppmv in 2004 [1]), sustainable fuel cells are a major topic for investigation.

Direct carbon fuel cells (DCFCs), which utilise elemental carbon as the fuel source, elicit significant attention. In addition to chemical robustness and ready availability from numerous sources, carbon has a high energy density (20 kWh/l c.f. liquid hydrogen 2.4 kWh/l) and the theoretical energy efficiency based on the overall cell reaction of Eq. 1:

\[ C + O_2 \rightarrow CO_2 \] (1)

even slightly exceeds 100% as a result of the entropy increase associated with the reaction [2].

DCFCs were first conceptualised in 1896 by W.W. Jacques [3]. The prototype employed molten NaOH/KOH as electrolyte at operating temperatures of 400–500 °C, with processes represented chemically in Eq. 2 or electrochemically at the carbon anode as Eq. 3.

\[ 2 \text{HO}^- + \text{CO}_2 \rightarrow \text{CO}_2^{2-} + \text{H}_2\text{O} \] (2)

\[ \text{C} + 6\text{OH}^- \rightarrow \text{CO}_3^{2-} + 3\text{H}_2\text{O} + 4\text{e}^- \] (3)

Carbonate buildup poisons the cell, requiring replacement of the electrolyte. However, addition of oxides (e.g. MgO) prolongs cell life to several months.

More recently, Pesavento [4] reported adding acidic oxides to decompose the carbonate and humidification of the fuel feed stream to keep a partial pressure of water above the melt, thereby converting the oxides formed in the decarbonation of the carbonate back to hydroxides. Experimentally, the basis for a coal-powered DCFC (http://www.sara.com/RAE/carbon_fuel.html) consists of a stainless steel Dewar flask, an anode basket housing caged carbon and employs a soluble oxidiser as cathode fed with humidified water.
Anbar and Weaver’s patent [5] uses alkali-metal molten carbonate electrolytes, with evolved CO₂ maintaining the electrolyte composition (Eqs. 4 and 5).

\[ \text{C} + 2 \text{CO}_2^- \rightarrow 3 \text{CO}_2 + 4 \text{e}^- \quad \text{anode} \quad (4) \]

\[ \text{O}_2 + 2 \text{CO}_2 + 4 \text{e}^- \rightarrow 2 \text{CO}_3^- \quad \text{cathode} \quad (5) \]

The fuel-rich molten electrolyte (40% Li₂CO₃/30% K₂CO₃/30% Na₂CO₃) floats on top of the molten lead anode. The electrolyte is prone to decomposition into oxides and CO₂, and CO₂ must be fed into the oxidant air stream to regenerate the electrolyte. The net result is a lower cell voltage. Additional problems with lower ionic conductivity of the carbonate electrolytes at the operating temperatures (650–750 °C) and corrosion of cell components render this carbonate system unviable.

Recent advances in molten carbonate fuel cell (MCFC) technology [6] for the electrochemical conversion of hydrogen have led to patents being issued by Cooper et al. [7, 8] for the direct electrochemical conversion of elemental carbon. The stability, ionic conductivity and thermal properties of carbonates for MCFC applications have been widely investigated since the 1960s, [9] and problems associated with excessive electrolyte evaporation and degradation have been tackled.

**Today’s technologies**

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Cooper’s group (http://www.llnl.gov/str/June01/pdfs/06_01.1.pdf) has focused on portable applications by...
Table 1 Results from different carbons at 700 °C

<table>
<thead>
<tr>
<th>Carbon type</th>
<th>Current density at 0.5 V (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>7.4 (650 °C)</td>
</tr>
<tr>
<td>Graphite</td>
<td>N/A</td>
</tr>
<tr>
<td>Charcoal (Halcan Brites)</td>
<td>N/A</td>
</tr>
<tr>
<td>Glassy carbon</td>
<td>6.7</td>
</tr>
<tr>
<td>Carbon black (super P)</td>
<td>5.0</td>
</tr>
<tr>
<td>Carbon black (super P formulated</td>
<td>2.2</td>
</tr>
<tr>
<td>for Li-ion batteries)</td>
<td></td>
</tr>
</tbody>
</table>

tailoring the particle size and morphology of the carbon fuel. Carbon reactivity was found to depend upon the degree of disorder in the lattice and the particle size. Problems with achieving stable cell voltages [10] were partially overcome by carbon tailoring.

To overcome problems with insufficient electrode wetting by the electrolyte, the horizontal planar geometry in Cooper’s initial patent [7] has been modified to a tilted cell design [8], see Fig. 1. In large-scale stationary MFC designs, the electrolyte level is controlled by capillary action, with auxiliary reservoirs of electrolyte controlling the carbonate coverage of the electrodes within the cell. Tilting the cell to ensure some coverage of electrode surfaces at all times reduces the overall effective area of the cell, as part of the surface is always above the electrolyte level.

The technical problem of introducing CO₂ into the oxidant air stream could be prevented by hydridising the fuel cell design and employing a solid oxide electrolyte to separate cathode and anode compartments. Oxygen is reduced to O²⁻ at the cathode and is transported across the solid electrolyte membrane to the melt where it combines with CO₂ released by the anode, regenerating the carbonate electrolyte without diluting the inlet gas feed. Thus, mechanical complications arising from the transfer of CO₂ from exhaust to inlet gas streams can be avoided. The use of a solid electrolyte also negates the need for a planar design.

CellTech power cell systems

The company’s technology is based around liquid tin anode solid oxide fuel cells (LTA-SOFCs; http://www.celltechpower.com/technolgy.htm) in which the tin anode is molten at operating temperatures. The electrolyte in these systems is typically yttria-stabilised zirconium oxide (YSZ), which, at high temperatures, is an excellent O²⁻ conductor. The YSZ is coated on one side by an electrically conductive ceramic cathode material, e.g. lanthanum manganese doped with strontium (LSM) and on the other side by a nickel/YSZ cermet anode (Fig. 2).

During cell operation, O²⁻ ions are extracted at the cathode and pass through the electrolyte to the anode (fuel) side, combining with H₂ or CO to form H₂O or CO₂. Meanwhile, electrons are released at the anode and travel through the load, producing electrical energy. Electricity is produced by oxidation at the anode to tin oxide (Fig. 3), which is reduced back to the metal by the fuel at the anode.

In current designs, the cathode is a support structure with a tubular configuration, although electrolyte supports and a planar geometry are possible.

LTA-SOFCs combine the efficiency and reliability of conventional SOFCs with an expanded range of useable fuels and exhibit several attractive features. LTA-SOFC stacks produce electricity directly from, e.g. diesel, coal, natural gas and plastic, as well as hydrogen. Other advantages include: no reformer or pre-reformer is required; no shift reactor or purifier is necessary; direct fuel utilisation increases system efficiency; coal, plastic and biomass can be used without a gasifier. Sulfur does not poison LTA-SOFCs. Furthermore, the anode stores chemical energy, allowing use
as an integral rechargeable battery, thereby reducing or eliminating batteries typically used for smoothing peak power. In addition, as precise control of air/fuel ratio is unnecessary, system control complexity is reduced.

St Andrews University/DSTL DCFC

DCFC research at St Andrews employs a cell design shown schematically in Fig. 4. Advantages of this design over other published types include: obviating the need for introducing CO₂ or H₂O into the oxidant gas stream; the cathode is never in contact with the electrolyte, avoiding corrosion; readily available materials are used in its construction. The eutectic mixture comprises 62.38% Li₂CO₃/K₂CO₃ and several carbon modifications (i.e. different surface areas) can be used successfully as fuels. Potentiodynamic measurements, taken over an operating temperature range of 550–800 °C, reveal promising current–voltage ratios.

Early studies in the St Andrews System [12, 13] have demonstrated encouraging results. Using high surface area carbons, it has been demonstrated that the cell is capable of yielding appreciable current densities (Table 1).

Environmental perspective

Fuel cell technology has the potential to offer high efficiency electrical power generation in a renewable economy (Fig. 5), with carbon fuel cells in particular delivering high energy densities. Although it is essential to reduce our net emissions of CO₂, carbon can still be an energy carrier. The systems discussed here have the potential to be environmentally neutral if they can utilise renewable carbon sources, e.g. fuels derived by pyrolysis of crop material [14]. The use of renewable fuels in such systems is not yet well established, but does have enormous potential.

Summary

The three technologies described in this paper are still in fairly early stages of development. The St Andrews DCFC system is still very much in its infancy and requires much effort to optimise current density. Although issues surround the stability of cell performance over extended periods, the potency of carbon as a fuel source, its ready availability from renewable sources or hydrocarbon cracking, CO₂ management by sequestration and ready scale-up, suggests a fruitful long-term future for DCFCs.

References