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# Answers to Frequently Asked Questions about Direct Carbon Conversion

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## Disclaimer

# ANSWERS TO FREQUENTLY ASKED QUESTIONS
# ABOUT DIRECT CARBON CONVERSION

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## 1. Carbon Efficiency

**a.** *Will all the carbon be converted into $CO_2$? Under what conditions will CO be formed?*
Under normal operating conditions, all the carbon is converted to $CO_2$ (n=4 electrons/mole-C). Under open circuit potentials, the voltage can be higher than that for the $C + O_2 = CO_2$ reaction, and represents a mixed electrode in which both $CO_2$ and CO are evolved. The open circuit potential can be as high as $1.3 - 1.4$ V, depending on temperature and whether a purge gas has been used to lower $CO_2$ activity. The anode must be polarized below the equilibrium potential for the $C + O_2 = CO_2$ reaction (i.e., 1.02 V at 750 °C), and this means a certain amount of current must flow. Vutetakis found that applied current densities of 110 mA/cm$^2$ resulted in $CO_2$ production at n = 4 in coal-powder salt slurries. Weaver reported the polarizations sufficient for n = 4 to be in the range of interest for efficient fuel cell operation. The requirement to polarize the anode means that the cathode polarization must be low if n=4 conditions are met with a cell voltage above 0.8 V.

## 2. Cathode Efficiency

a. *Will all of the $CO_2$ exit as a "pure gas" or will some of it go off with the spent air? If so how much?*
The anode produces 3 moles of $CO_2$ for each mole of C consumed. Of the 3 moles, two are recycled with the air flow. One can design the air flow distribution so that the loss of $CO_2$ (unconsumed by the cathode) may be arbitrarily low, but 80% efficient flows are often obtained. This means that 40% of the net production of $CO_2$ is lost with the air and 60% emerges from the anode in pure form. If it is important to capture all of the $CO_2$, two routes may be considered: condensing from the air cathode exhaust or operation on oxygen/$CO_2$ mixtures. The latter would greatly increase power density of the cell, reduce cost per kW, and is an option broadly considered by fuel cell developers as the cost of membrane separation continues to fall.

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3. **Electrolyte Stability**

   a. ***Is the electrolyte stable under operating conditions?***
      Yes, the mixtures of alkali carbonates we use are chemically stable. There is a tendency of the salt to evaporate, which is offset by condensation on cooler parts of the fuel in, for example, the feed train. Electrolyte composition is invariant—a requirement for any fuel cell.

   b. ***How often must the electrolyte be replaced?***
      If fuels are used that have impurities (such as ash), these impurities will accumulate in the melt, eventually rendering them incapable of supporting the current. Weaver (SRI) found that accumulation of ash to levels up to 10%-wt had no discernable effect on cell performance. The time required to accumulate 10% ash (in days) is *very roughly* equal to 1/f, where f is the mass fraction of ash in electrolyte. Thus for deep cleaned coal having 0.17% ash, the electrolyte must be replaced at intervals of 588 days. A practical way of stabilizing electrolyte against ash accumulation is to continuously drain electrolyte from the cell into a sump and wicking the liquid fraction back into the cell. This would greatly extend the life of the electrolyte.

   c. ***What options are there for electrolyte replacement?***
      We would prefer to operate with a eutectic mix of K and N carbonates, which is possible above temperatures of about 710 °C. The $K_2CO_3$ and $Na_2CO_3$ could be separated with high efficiency from the contaminated melt with low cost aqueous salt dissolution and recrystallization processes.

   d. ***What is the fate of sulfur in fuels, if present?***
      In the anodic reaction of turbostratic carbon containing sulfur in the Hall process for making aluminum, the sulfur emerges as COS, which rapidly decomposes upon contact with air to form $CO_2$ and $SO_2$. The $SO_2$ can be readily separated from the otherwise pure $CO_2$.

   e. ***Can the separator be protected against fouling?***
      There is no net reaction of the carbonate electrolyte during cell operation. However, the cell reactions generate a strong and continuous flux of carbonate from cathode to anode. Carbon dioxide is added to the air stream where it reacts as part of the cathode electrochemistry: $O_2 + 2CO_2 + 4e^- = 2\ CO_3^{2-}$. The carbonate produced fluxes continuously through the electrolyte phase of the separator at flux equal to i/2F. The electrolyte flux tends to remove any material that might diffuse or be transported into the separator. In the anode reaction, the carbonate reacts with the carbon, $C + 2CO_3^{2-} = 3CO_2 + 4e^-$. The net reaction is $C + O_2 = CO_2$. The steady state composition of the electrolyte will be determined by the relative mobility of the various cations in the melt.

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## 4. Corrosion Issues

a. ***Corrosion by sulfur.***
Corrosion by sulfur of metals such as nickel or copper by spalling processes severely limit the number of materials that can be used in the anode side of the fuel cell. We believe we can construct the anode compartment completely with materials that are not subject to spalling corrosion, such as high-temperature fired graphite and vitreous carbon, dense alumina, and zirconia.

b. ***Steam corrosion and hydrogen embrittlement.***
The carbon fuel, once delivered to the cell, is anhydrous. Consequently we expect no problem with either steam corrosion or hydrogen embrittlement, which have plagued development of hydrogen fuel cells using the same molten carbonate electrolytes.

## 5. Heat Transfer Considerations

a. ***How is operating temperature maintained?***
On scales of about 1 kW and above, operating temperature is readily maintained by the waste heat generated by the cell. Even at 80% HHV conversion efficiency, active heat rejection is required on the large scale.

b. ***How is the system initiated and shut down (initial heat- up and cool down).***
The initial heat-up of the system involves either combustive gas and/or electrical resistance heating.  The bipolar graphite plates and adjacent carbon fuel could be electrically heated to bring the system up to temperature. The energy cost of heating up an initial carbon charge is a few per cent of the HHV of the carbon. Graphite and elemental carbon have some of the highest thermal diffusivities of common materials, somewhat simplifying startup by promoting rapid thermal equilibration. Once hot, the thermal inertia of carbon, alumina and firebrick insulation can be used to maintain temperature, with heat losses regulated by the loss through the firebrick. The problem of initial heat-up is not dissimilar to the initial heating of any high temperature combustion process that requires a slow approach to thermal equilibrium to prevent mechanical stress and potential damage to the hardware.

## 6. Alternative Electrolytes

a. ***Doesn't the DCFC require electrolytes containing expensive $Li_2CO_3$?***
Much of our work has been done in the eutectics developed for the

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hydrogen molten carbonate fuel cell (MCFC) using $Li_2CO_3$ with Na or K carbonates. This is required for the low temperatures sought for the MCFC (650 °C). DCFC for the most part requires temperatures of about 750 °C. This allows use of the less expensive and more easily recycled $(Na,K)_2CO_3$ eutectic composition. The downside of this is that the chemistry and catalysis of the air electrode were developed for the lower temperature eutectics and will have to be modified for the higher temperature. The upside of this that there are many excellent catalysts effective at 750 °C that were developed for and not used by the MCFC at 650 °C.

b. ***Isn't the carbon/caustic Jacques Cell a superior alternative for DCFC?***
   In the late 19th century, William Jacques performed impressive demonstrations of a carbon/caustic battery at temperatures of 300-400°C in a simple rod-and-can configuration and on scales of over 10 kW. Jacques reported that his battery sustained the reaction, $C + 2NaOH + O_2 = Na_2CO_3 + H_2O$.  The technology has no relevance to conversion of fossil fuels and was quickly abandoned for three related reasons:
   i. <u>The Jacques cell is not a fuel cell</u>. As NaOH (and KOH) are consumed to make $Na_2CO_3$ (or $K_2CO_3$), the melt either freezes or the temperature rises to the eutectic m.p. (710 °C for $(Na,K)_2CO_3$). Thus, as he reported, the Jacques cell devolves to a molten <u>carbonate</u> cell such as we are proposing, and any transient benefits of low temperature operation are quickly lost.
   ii. <u>The cost of caustic is prohibitive</u>.  Each ton of coal (costing $30) requires the consumption of 6.7 tons of NaOH (or 9.5 tons of KOH) costing $2000 (or $7600 for KOH). The approach has no economic feasibility.
   iii. <u>The efficiency is poor</u>. The theoretical voltage of the Jacques cell is 1.4 V because of the energy degradation inherent in the exothermic conversion of the caustic to the carbonate.  At reported voltages of 0.6 V, the efficiency is no better than an advanced coal burning power plant, but far more expensive.
   The Jacques cell thermodynamics was thoroughly analyzed by Cairns[1]. At various times, attempts have been made to revitalize the technology with questionable schemes to allow carbon to evolve $CO_2$ in the presence of caustic without the acid/base reaction producing $Na_2CO_3$.  To our knowledge, the schemes have not been shown to be successful, and no serious efforts exist today to revitalize the Jacques cell.

c. ***What about Direct Carbon Conversion using a solid ceramic electrolyte?***
   This is an old concept that we examined in on the basis of work reported between 1987 and 1999 before starting the carbonate based research. Carbon and ceramic electrolytes (e.g., defect zirconia) are both solids, so

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[1] H. A Liebhafsky and E. J. Cairns, Fuel Cells and Fuel Batteries (John Wiley and Sons, New York, 1968).

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the carbon may make only a point contact with the electrolyte, not over an extended surface as in a liquid electrolyte. As a consequence, the electrochemically active substance is CO—formed in situ by the Boudouard reaction of $CO_2$ with carbon over its extended surface. The CO discharges at the solid electrolyte surface. The problem here is utilization: the continuous dilution of the electro-active species CO by the product $CO_2$ means the chemical potential of the fuel <u>in the steady state</u> drops below cell voltages necessary for efficient discharge. The same problem in hydrogen fuel cells at high temperatures (where steam lowers the hydrogen chemical potential) leads to practical utilizations of only 80-85%. An excellent thermodynamic treatment of the limitations of this approach can be found with Nakagawa et al.[2] and in the papers by Hemmes and Au at the Technical Institute of Delft. Ihara[3] conducted experimental work in solid oxide fuel cells using defect zirconia conductors.

7. **Comparison with hydrogen fuel cells**

   a. ***It took decades to develop the MCFC. Why do you expect a rapid reduction to practice of the DCFC?***
   There are several reasons for a more rapid development of the Direct Carbon Fuel Cell than high temperature hydrogen fuel cells. (1) The melt-saturated carbon fuel is not explosive and reacts only slowly in air. As a consequence, our fuel cell designs have no need for gas-tight seals between air chamber and anode chamber. This obviates a major barrier that the MCFC had to overcome. (2) The DCFC system is anhydrous. This obviates having to find solutions to major corrosion issues of hydrogen fuel cells, i.e., steam corrosion of metals at high temperatures and hydrogen embrittlement of metals. (3) Catalysts developed for the MCFC are applicable to the DCFC as well, and a wide variety of catalysts studied for high temperature air- or oxygen depolarized fuel cells can be used at the higher temperatures of the DCFC. (4) The steam reforming of fuels is obviated for the carbon fuel cell. Pyrolysis is simpler and lower in cost than steam reforming, particularly if the carbon is wetted with a molten salt that prevents agglomeration. (5) The refueling of carbon fuel cells is likely to be less difficult than the refueling of hydrogen fuel cells. In addition to the non-explosive nature of carbon, the volume energy density of carbon is 15,000 times that of hydrogen, meaning that the volume rate of transport of carbon is lower than that of hydrogen by a factor of 15,000.

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[2] N. Nakagawa and M. Ishida, 1988,Performance of an internal direct-oxidation carbon fuel cell and its evaluation by graphic exergy analysis, Ind. Eng. Chem. Res., 27 (7).

[3] Ihara, Manabu; Keisuke Matsuda, Hikaru Sato, and Chiaki Yokoyama, 2003, Solid State Fuel Storage and Utilization through Reversible Carbon Deposition of a SOFC Anode, Paper 14th International Conference on Solid State Ionics, Monterey, USA, June 22-27.

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Transport of carbon particles by entrainment in an inert gas (e.g., $CO_2$) is commonplace in the domestic carbon black industry that transports 5 million tons per year by this technique. (6) The hydrogen fuel anode catalyst is sensitive to sulfur poisoning at concentrations as low as 0.5 ppm—a major barrier to production of fuels and life of cell. In contrast, the carbon fuel cell uses no anode catalyst, and sulfur has no effect on anode efficiency. An important byproduct of working with carbon fuel cells is that the carbon anode electrochemistry lends itself to the operation of very large anodes, which means fewer components. A typical Hall cell uses turbostratic carbon anodes of many square meters area.

b. ***The concept of a carbon fuel cell has been around for a long time. After all these years what has LLNL added to this technology that makes it a "winner"?***
We clearly identified a relation between anode disorder on the nanoscale and anode reactivity, which allows us to select fuels from a wide range of hydrocarbons pyrolyzed at a low temperature and a low cost. Until we combined a gas-diffusion cathode with a paste carbon anode in 1999, no one had ever actually demonstrated a practical carbon/air fuel cell. Impressive studies done by Hauser, Vutetakis, Weaver, and others were limited to tests of half-cell anodes that produced no net energy. The work by Jacques did not produce a fuel cell, but an expensive fuel battery. While the concept of "electricity direct from coal" is over a century old, we were the first to demonstrate a carbon/air cell that generated power using a practical gas diffusion electrode similar to that employed by the molten carbonate fuel cell.

c. ***$H_2$ fuel cells are expensive to build, maintain and have serious corrosion problems. Why should we expect DCFC to do much better?***
As stated above, the carbon fuel cell is anhydrous. Therefore the serious corrosion issues facing the molten carbonate fuel cell (steam corrosion, hydrogen embrittlement of metals) do not apply to the carbon fuel cell. With fuels having sulfur, DCFC is severely limited in low cost materials of construction on the anode side. Fortunately, our designs use only unreactive graphite and dense alumina, which are immune to sulfur corrosion. The hydrogen fuel cell needs (MCFC or SOFC) have anode catalysts that are readily poisoned by sulfur at levels as low as 0.5 ppm. In contrast the DCFC uses no anode catalyst other than the surface of the carbon electrode, which is continuously regenerated. Finally, a major factor in the cost of the hydrogen fuel cell is the reformer and purifier of the hydrogen fuel—factors obviated by carbon fuel cell.

d. ***How does the effective power density of DCFC compare to $H_2$ based fuel cells?***

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At this writing, we have produced a number of cells with power densities typically 0.8-1 kW/m² at 0.8 V. This is lower than MCFC and SOFC that typically produces power at 4 kW/m², based on the active area of the stack. Several factors make a direct comparison here almost meaningless. (1) High temperature fuel cells typically use a stack with electrodes spaced and supported by orthogonal ribs, with the area between the ribs (30-40%) being active. Thus the power density of 4 kW/m² is only 1.2-1.6 kW/m² when referenced to the area of the cell. In DCFC the full area of the cell is used. (2) Currently, the polarization of the carbon anode is very low (0.4 ohm-cm²), and nearly all of the polarization of the cell (3-4 ohm-cm²) is associated with the resistance of the cathode. Thus the cell is limited in power due to poor performance of the air cathode. The cathodes we have been using have a fine porosity developed for MCFC applications having a fixed electrolyte inventory, and readily flood under the excess electrolyte conditions required by the DCFC. They need to be redesigned with a more open structure appropriate to DCFC to prevent cathode flooding. When this is done, we expect power densities per unit of active cell area to be comparable to those of high temperature hydrogen fuel cells. (3) The only interest one has in comparing power densities is that it is an indication of stack cost <u>for similar fuel cells</u>. DCFC and hydrogen fuel cells are quite dissimilar, and DCFC uses lower cost materials (porous or dense alumina; high-fired graphite); our cost estimates of $500/m² and $500/kW (at 1 kW/m²) are based on the cost of commercial materials in large-scale production.

8. **Off gas Cleanup**.

    a. ***How will any impurities in the fuel be handled? Would it be easier/harder than in existing plants?***
    It appears that existing technologies for chemically de-ashing coal are adequate to remove impurity entrainment from a serious consideration in system operating cost. One process uses variants of the Bayer chemistry to digest silica-based ash and produces a product of 0.17% ash for $3/GJ. Another process produces ash at levels of 200 ppm for $2/GJ, but utilizes only 60% of the coal; the balance is burned in conventional plants without loss of energy content. This is an open area of research, and the cost of pre-cleaning the coal must be balanced against the economics of cell operation and life of the electrolyte. The offgas impurities, chiefly sulfur, present the same problems in clean up as from conventional plants. These de-ashing technologies were developed for making a solid particulate gas turbine fuel, and no doubt less expensive techniques can be developed for the less-demanding DCFC fuel.

    b. ***Why does DCFC have such a high electrical efficiency vs. all other fossil fuel (and H$_2$ based) electrical generating plant?***
    The carbon fuel cell derives its high efficiency at practical rates from three fundamental aspects of the reaction. First there is essentially no entropy

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change in the $C + O_2 = CO_2$, so that theoretically all of the heat of combustion of the carbon (at 750 °C) may be converted to electric power (cf. only 70% for hydrogen fuel cells at the same temperature is theoretically accessible in the cell). Second, the activities of carbon and $CO_2$ product are invariant, so 100% of the carbon fuel that enters the cell is consumed to make electric power (for gaseous fuel cells at 750 °C, only about 80% is convertible under practical conditions). Finally induced disorder in the carbon structure allows these high efficiencies to be achieved at practical rates (100 mA/cm$^2$), at which 80% is delivered as power. Thus the efficiency of the carbon/air cell is 80% under conditions where the efficiency of the hydrogen cell is below 50%.

9. **What are the major technical challenges for DCFC being proposed by LLNL? Are they engineering and scale-up or are fundamental scientific breakthroughs required?**
    *a.* We believe that the development of practical, low-cost applications of direct carbon conversion is a challenging but straight forward effort involving engineering and materials selection. The fundamental science behind this is sufficient to support engineering development at this point.
    b. The development and demonstration of self-feeding wedge shaped cells using particles of carbon or rigid plates.
    c. The redesign of the gas diffusion electrode with a more open, higher porosity structure as required for the excess-electrolyte mode of operation of DCFC, and the optimization of the choice among available catalysts.
    d. The redesign of the cathode for use of the $(Na,K)_2CO_3$ molten salt rather than salts containing the more expensive $Li_2CO_3$
    e. The development or selection of materials for interconnects between the graphite bipolar plate and the NiO-Li catalyst (including support for same) of the adjacent cell. Such materials are known but down-selecting requires experimentation.
    f. The maintenance of wetting of the carbon fuel by the molten salt, and the conservation of salt in the system against wicking out of the cell or losses by evaporation.

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