

Direct Electrochemical Conversion of Carbon: Systems for Efficient Conversion of Fossil Fuels to Electricity

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This article was submitted to Fuel Cell 2000 Seminar, Portland, OR,
November 2, 2000

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

August 10, 2000

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This work was performed under the auspices of the United States Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

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**DIRECT ELECTROCHEMICAL CONVERSION OF CARBON:
SYSTEMS FOR EFFICIENT CONVERSION OF FOSSIL FUELS TO ELECTRICITY**

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The direct electrochemical conversion of carbon involves discharge of suspensions of reactive carbon particles in a molten salt electrolyte against an oxygen (air) cathode. (Figure 1). The free energy and the enthalpy of the oxidation reaction are nearly identical. This allows theoretical efficiencies ($\Delta G(T)/\Delta H$) to approach 100% at temperatures from 500- to 800 °C. Entropy heat losses are therefore negligible. The activities of the elemental carbon and of the carbon dioxide product are uniform throughout the fuel cell and constant over discharge time. This stabilizes cell EMF and allows full utilization of the carbon fuel in a single pass. Finally, the energy cost for pyrolysis of hydrocarbons is generally very low compared with that of steam reforming or water gas reactions.

Direct electrochemical conversion of carbon might be compared with molten carbonate fuel cell using carbon rather than hydrogen. However, there are important differences. There is no hydrogen involved (except from trace water contamination). The mixture of molten carbonate and carbon is not highly flammable. The carbon is introduced in as a particulate, rather than as a high volume flow of hydrogen. At the relatively low rates of discharge (about 1 kA/m²), the stoichiometric requirements for carbon dioxide by the cathodic reaction may be met by diffusion across the thin electrolyte gap.

The history of carbon/air cells and batteries dates from the nineteenth century. William Jacques (1896) operated unseparated cells using sintered coke electrodes, iron cathodes and an electrolyte consisting of molten hydroxides (1,2). Air was sparged through the electrolyte. Rates were reported as high as 115 mA/cm² at 1 Volt and 82% utilization efficiency. However, molten hydroxides were limited by their eventual conversion to carbonates because of the production of CO₂ within the melt. These devices were primary batteries, not fuel cells, as the electrolyte was not invariant but was progressively consumed to form sodium carbonate. Furthermore, Haber (3) later showed that the carbon electrode in Jacques' system probably acted as a hydrogen electrode because of the instability of the electrolyte—production of H₂ from KOH.

Significant work on coke/molten-carbonate/oxygen(air) was done by Weaver et al. (4-6) in the late 1970's. This work focused on chemically stable electrolytes of alkali carbonates and on rigid, sintered electrodes made of various cokes, devolatilized low-ranking coals, graphite and spectroscopic carbon. They reported that the coulombic efficiency of carbon anode dissolution in molten carbonate approached 100% at T < 800 °C for the cokes. The highest reactivity (anode overpotentials of 0.2 V vs. OCP at 1 kA/m²) was obtained with calcined low-ranking coals. Voltages from completed C/O₂(air) cells were not reported. However, the energy and economic cost of electrode fabrication, the logistics of electrode distribution among cells and the entrainment of ash into the melt (causing its solidification) curtailed practical applications.

Vutetakis conducted studies of carbon/molten-carbonate half-cell configurations, using a stirred electrolyte of mixed alkali carbonates (e.g., (Na,Li,K)₂CO₃) with 5-25%-wt additions of carbon granules derived from coals, graphite and charcoal sources (7,8). His configuration did not provide high current densities on the gold-wire anode current collector: anode overpotentials of 0.2 V were found with current densities below 20-30 mA/cm². No complete C/O₂(air) cells were tested. The work confirmed Weaver's results in coulombic efficiency, but showed that the

Boudouard corrosion reaction of the carbon ($C + CO_2 = 2CO$) occurred and required minimization of the dead volume in the melt.

We report recent experimental work at LLNL using melt slurries of reactive carbons produced by the thermal decomposition of hydrocarbons. We have found that anodic reactivity of carbon in mixed carbonate melts depends strongly on form, structure and nano-scale disorder of the materials, which are fixed by the hydrocarbon starting material and the conditions of pyrolysis. Thus otherwise chemically pure carbons made by hydrocarbon pyrolysis show rates at fixed potentials that span an order of magnitude, while this range lies 1-2 orders of magnitude higher than the current density of graphite plate electrodes. One carbon materials was identified which delivered anode current densities of 1 kA/m^2 at 0.8 V (i.e., 80% efficiency, based on the standard enthalpy of carbon/oxygen reaction, and assuming full conversion), which we believe to be sufficiently great to allow practical application in fuel cell arrays. Since the hydrocarbon starting materials are "ash free," entrainment of ash into the melt is not limiting. Finally, the use of fine carbon particulates in slurries avoids cost and logistics of carbon electrode manufacture and distribution.

The motivation for this research is to define a route for the use of broad fossil fuel resources in electricity production that meets the efficiency requirements of the "21st Century Fuel Cell" goals set by the Department of Energy through National Energy Technology Laboratory. The evolution of carbon dioxide as a pure, anhydrous gas from the anode compartment allows an option for sequestration without subsequent chemical processing. One of several such routes involves the pyrolysis of heavy petroleum fractions into separate streams of carbon and hydrogen, and the (full) consumption of both in their respective fuel cells. Using single pass carbon cells and without the use of turbine bottoming cycles, we show that efficiencies of over 70% (HHV) are achievable at rates that are practical for base load power generation applications. Higher efficiencies with heat engine bottoming cycles, or feedback of cell waste heat to assist the pyrolysis, are also possible.

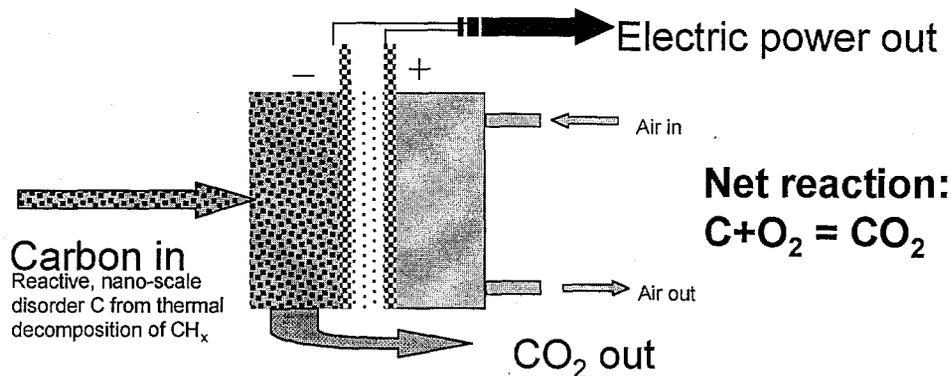


Figure 1. Shown is a schematic of a "direct carbon conversion" cell, or carbon fuel cell. Carbon is introduced into a molten carbonate mixture to form a particulate slurry. Carbon dioxide is evolved as a pure substance from the anolyte. Rates as high as 1 kA/m^2 at 0.8 V (~80% efficiency, based on ΔH_{298}° of $C + O_2 = CO_2$) have been achieved using certain pyrolyzed hydrocarbons.

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This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.