LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-TR-738382

Development and Demonstration of Carbon Fuel Cell Final Report CRADA No. TC02091.0

J. F. Cooper, J. K. Berner

September 12, 2017

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Development and Demonstration of Carbon Fuel Cell

Final Report
CRADA No. TC02091.0
Date Technical Work Ended: April 30, 2007

Date: June 24, 2007 Revision: 2

A. Parties

This project was a relationship between Lawrence Livermore National Laboratory (LLNL) and Contained Energy, Inc. (CEI).

The Regents of the University of California
Lawrence Livermore National Laboratory
7000 East Avenue
Livermore, CA 94550
John F. Cooper
Tel: (925) 423-6649
Fax: (925) 422-6892

Contained Energy, Inc.
2980 Fontenay Road
Shaker Heights, OH 44120
J. Kevin Berner
Tel: (216) 973-1762
Fax: (216) 283-5148

B. Project Scope

This was a collaborative effort between The Regents of the University of California, Lawrence Livermore National Laboratory (LLNL) and Contained Energy, Inc. (CEI), to conduct necessary research and to develop, fabricate and test a multi-cell carbon fuel cell.

The work proposed under this CRADA is intended to resolve issues concerning the air cathode structure and support, separator wetting with molten salt, and gravity feed of the anode material within sealed cells. Success in developments early in the project will allow construction of a multi-cell stack comprised of five cells in bipolar series connection with operation as a fuel battery.

We intended to demonstrate the discharge of a five-cell stack with bipolar construction as the major accomplishment of the project, with demonstration of operation for a period of 100 hours. This demonstration was not achieved because of unforeseen problems in the stability of the zirconia fabric separator and of a tungsten-copper bronze air channel designed to match the thermal properties of dense alumina frame. These problems prevented successful assembly of the

alpha 1 single cell that was prerequisite to proceeding to a 5-cell alpha 2 prototype including bipolar series connection plates.

Nonetheless significant technical successes were achieved in critical technologies: (1) a technique of *in situ* formation and activation of lithiated nickel oxide catalyst was researched and successfully developed, matching electrical properties reported in literature; (2) a low-cost, high tolerance alumina frame design was developed and procured for tests here and subsequently at CEI; (3) by inspection of vertical separators following discharge of 150-cm^2 cells, the baseline yttria-stabilized zirconia (YSZ) separator was found to maintain wetting over hydrostatic heads of at least 10 cm—a prerequisite for the cell designs of the alpha 2 modules; (4) the ability of the carbon particle bed (saturated with molten salt) to fall under its own weight and conform to the interior geometry of the anode chamber of the alpha 2 design was found experimentally; (5) sufficient conductance (0.4 -cm) of the carbon anode bed (for high conductivity anode fuels) was shown for dimensions comparable to anode bed thickness with voltage drops of 40 mV at 100 mA/cm^2.

In all, successful development of a 5-cell alpha 2 prototype required success in all of 12 major technical challenges that were identified prior to the CRADA. We were able to achieve success (or define a route to same) in 10 of the 12 problems, but progress towards the Alpha 2 demonstrations was sharply curtailed because of separator and air channel instability.

This project consisted of the following major tasks, subtasks, and deliverables:

Task 1. Test Setup (LLNL/CEI).

Task 2. Single Cell System Test (LLNL/CEI). Duration: Months 1 through 5

LLNL will be responsible for the development of a single cell prototype. LLNL will resolve issues of cathode structure and activation, maintenance of wetting of the separator, and conductivity of the anode bulk which transfers current generated near the separator to and through the graphite bipolar block. Laboratory cells are not expected to last indefinitely. LLNL and CEI will conduct post-mortem analyses on the cells after tests that will generally result in the destruction of the cells. CEI will provide the commercial manufacturing knowledge for the single cell design of the prototype and the test plan. CEI will procure and deliver to LLNL test cells, components, specialized test equipment and chemicals specified by LLNL for use in Task 2.

Task 3. Single Wedge Cell Test (Alpha 1) (LLNL/CEI.)
LLNL will take what was learned from the second task (mainly separator and cathode specifications) and apply it to the design and evaluation of a wedge-shaped cell that feeds fuel from an internal hopper, making this a single cell a "fuel battery." Feasibility of gravity feed (possibly with a weighted anode) is established. LLNL will verify that the voltage loss in the anode and anode/bipolar plate assembly is sufficiently low for stacking the cells.

CEI will provide the commercial manufacturing knowledge for the single wedge cell design of the prototype and the test plan. CEI will procure and deliver to LLNL test cells, components, specialized test equipment and chemicals specified by LLNL for use in Task 3.

Task 4. LLNL. Battery Stack Test (Alpha 2) (LLNL/CEI. Duration: Months 4 through 9

LLNL will combine wedge shaped cells into a series-connected, bipolar configuration of five (5) cells. The technology advanced in this stage is continuous feed of the stack. LLNL will assemble cells of the design perfected in Task 3 into a series-connection, with adjustment of the electronic and flow control to accommodate the larger size. With the larger number of cells, sealing problems, alignment of cells, and control of inter-cell shunts currents will be the new technical challenges.

The cell will also consist of a hopper that stores unreacted fuel for delivery to the cell. The hopper will consist of one or more plates of dense alumina having broad slots that communicate with the cells. This simple design should meet thermal requirements for heat rejection on this scale (75-150 W deliverable electric power).

At the end of the task, a successfully tested five-cell fuel battery stack directly indicates an approach to a fuel cell, i.e., with additional provisions for adding fuel to the stack under load and without altering the temperature of the cell. The choice of wedge cell and bipolar configurations was made, in part, with the objective of allowing a straightforward alteration of the system into that of a fuel cell.

CEI will provide the commercial manufacturing knowledge for the battery stack design of the prototype and the test plan. CEI will procure and deliver to LLNL test cells, components, specialized test equipment and chemicals specified by LLNL for use in Task 4.

Task 5. Final Report and Abstract (LLNL/CEI) Duration: Month 10

LLNL will draft the technical accomplishments of the project and submit to CEI for review. CEI will draft and provide LLNL with a summary of the commercial manufacturing aspects of the project. LLNL and CEI will work together to prepare and submit the final report and abstract within thirty (30) days of completion or termination of the project, as required under Article XI of the CRADA.

Deliverables:

1. Test Setup
2. Single Cell Test System
3. Single Wedge-Cell Test (Alpha 1)
4. Battery Stack Test (Alpha 2)
5. Final Report and Abstract

This CRADA was originally designated as a nine (9) month project. A no-cost time extension was executed for this CRADA, extending the expiration date to April 30, 2007. The project began in the second week of February 2006, and laboratory research was substantially complete by December 2006; addition tests were undertaken in presence of CEI personnel in March 2007.

C. Technical Accomplishments

The project was conducted on the basis of the schedule shown (in abbreviated form) in Table 1.1. It provided for an early freezing of an Alpha 1 design and materials less than six weeks following project start. A design review was conducted at LLNL on March 3, 2006, at which time engineering materials and design was frozen. The assembly of alpha 1 cells into a stack ("Alpha 2 prototype") was to begin 2 months before completion of the component testing ("single cell tests"). The project schedule was paced to deliver a fully engineered 5-cell stack (called Alpha 2 prototype) design early in the project. This necessitated placing in parallel (1) component research and development and (2) engineering, procurement and fabrication, rather than in series as proposed by LLNL for this CRADA.

Table 1.1 Schedule (condensed) for the project

Task	First Quarter	Second Quarter	Third Quarter
1. Test setup	xxxxxxxxxxxx		
2. Single cell	xxxxxxxxxxx	xxxxxxxxxxxxxx	
3. Alpha 1	xxxxx	xxxxxxxxxxxxxxxxx	
4. Alpha 2		xxxxxxxxxxxxxxxxx	xxxxxxxxxxxxxxxxx

This approach entails enhanced technological risk (relative to a schedule that would subordinate engineering design to prior and successful demonstration of each component). Nevertheless, significant technical accomplishments were made and are summarized in the chart of Table 1.2. I have designated each of the problem areas with a +, 0, or – sign designating, respectively, success (goals met); problems identified together with route to mitigation (but not implemented); and problems encountered and not resolved. LLNL either solved or identified a route to solution of 10 out of 12 problem areas. LLNL did not anticipate problems with separator stability or channel corrosion, the solution of which and their implementation in an Alpha 2 prototype required more time and resources than provided by the CRADA.

The specific technical accomplishments of this project are discussed with reference to Table 1.2

1. Air Cathode and Support Structure Development. Significant success is noted for the development of the air cathode, which was deemed the most critical unsolved problem prior to the CRADA. A method of fabrication of the cathode (time, temperature and composition profile) was developed that resulted in minimal polarization and in a high degree of electronic conductivity (0.2 ohm-cm)—matching the best results from in the catalyst literature. There remains to be done some optimization work involving increased reactive area of the cathode catalyst and configuration of current collector in order to meet technology limits of 30-50 mV total polarization relative to open circuit at 0.1 A/cm^2.

The Alpha-1 hardware did not allow positioning a reference electrode with Luggin capillary tube perpendicular to the surface of the cathode. We solved the problem by placing a length of YSZ fabric against the metal channel and a gold wire between the fabric and the frame wall, such that air flowed through from channel to make contact the wire and the fabric, wetted by molten salt, completed the circuit from reference electrode to cathode and support.

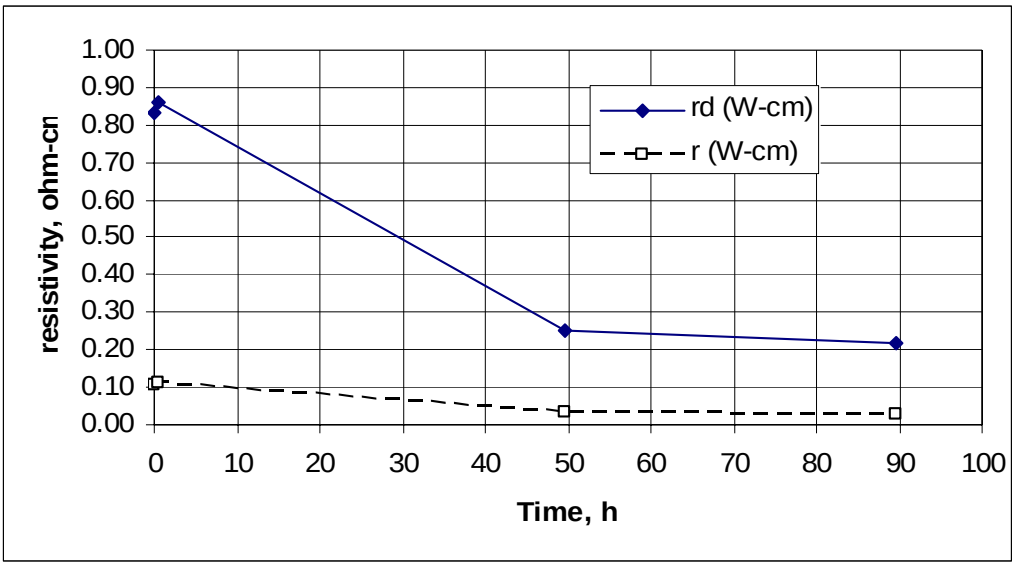

Figure 1.1. Air cathode catalyst resistance as function of time in presence of lithium carbonate potassium carbonate fused salt. Rd is measured resistance, in units of Ω-cm; r is extrapolated to theoretical density, taken to be equal to rd divided by solid fraction.

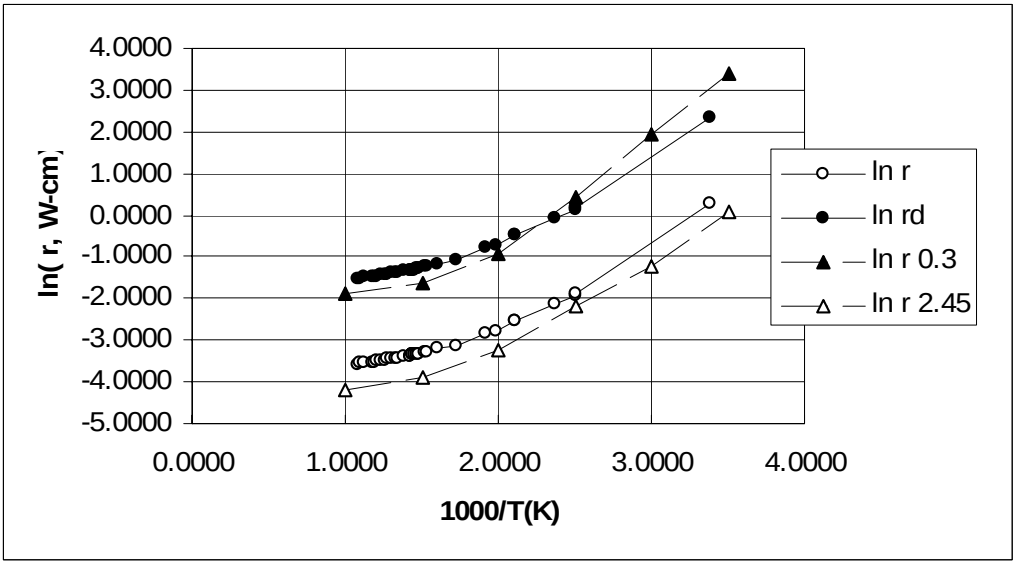

Figure 1.2. Resistance as a function of reciprocal temperature is shown. Closed and open circles represent resistance of mature catalyst prepared under the CRADA as measured and with correction for solid fraction, respectively. Our data is bound by closed and open triangular data points, representing the data at lithium concentrations of 0.3 and 2.45 mol %, respectively, according to Bosman (1965).

Table 1.2 Problems encountered and disposition in the CRADA, relevant to Alpha prototype development

No/ code		***Component***	***Problems***			***Notes***
			Prior to CRADA	*Encountered or solved during CRADA*	*Remaining after CRADA*	*Problems solved or identified*
1	+	Cathode	Poor conductivity and contacting; Unstable catalyst support; high electrode polarization	Problems in placement of reference electrode	Minor optimization of area, support	Problem solved: procedure developed for achieving low resistance and low polarization of catalysts on prototype scale
2a	0	Separator	None identified; expected separator resistance to be 2x melt resistance, ~0.8 Ω-cm	Increase in resistance of melt-wetted separator by factor of 10 over 4 days; increase in resistance of alpha 1 separator to 13.2 Ω-cm; in one case, disintegration to triclinic upon cycling.	Problems associated with lack of consistency in phase structure in different deliveries of the fabric from manufacture are believed possible for at least some instability	Problem does not account for all of high resistance of cell; routes defined to stable $LiAlO_2$ & YSZ fabric; short duration duty cycles may circumvent this issue.
2b	+	Separator wetting	Not known if separator remains wetted to height of cell (10 cm)	--	--	Examination of separators removed from full-scale cells showed melt retention over heights of 10 cm; also positive pressure of Ar flow maintained without leak to cathode.
3	+	Anode current collector (ACC)	Materials stability in anode environment	Corrosion of Ni above melt line in CO_2 atmosphere, but remains pliable below surface of carbon/salt bed	Developer needs to choose ACC material from available materials identified in literature (see notes)	Inconel, 304 and 316 SS are resistant to corrosion; absence of S is critical; materials sufficient for CEI first applications. Recommend consideration of Nitronic (high Mn) SS, which develop conductive films.
4	+	C/S/A sealing	No clear choices of cements and glasses	Leakage about cathodes	Problems solved; Minor optimization of cements on C/S/A	Problem appears solved. Diverse cement products and manufacturers were identified.
5	+	Cell Containment Materials	Scale up not investigated	Source; shrinkage; tolerances	Cost, weight	Problem solved: Frames manufactured to tolerance and provide reliable base for tests
6	+	C/S/A assembly	Non-reproducibility of configuration due to assembly errors	Large scale loss of contact	Means of compressive loading to maintain C/S/A contact over area	Possible solution: Invention made of cylindrical loading of rectangular C/S/A assemblies

7	0, +	Anode conduction	Not investigated; relied on anode current collector placed adjacent to separator	Wedge design requires low IR drop from separator to bipolar plate over distance of ~ 1 cm	Resistance of wetted particle bed sufficient for bulk; need data on bed/plate contact resistance and mode of conduction in bed	Problem addressed: Bed conductivity at elevated T in salt is sufficient in experiment which measured combined electrolytic and electronic conductivity.
8	+	Anode feed	Limited data on ability of anode bed to conform to cell under gravity load save in 1" diameter tubes of 3" height.	In alpha cell, we found anode fell under own weight and conformed to cell; Promotion of rapid wetting of fuel with molten salt and a tendency to float were noted.	Feed from hopper to cell must be addressed; possible formation of voids or bubbles in stationary cells should be investigated.	Anode bed wetted with salt is sufficiently fluid at 750 C to fall and conform; tapping of cell results in occasional improvement, indicating possible formation of small voids in cell.
9	-	Cathode channels	Not investigated	Catastrophic corrosion of W-0.2 Cu; units replaced by stainless steel channels (limited success)	Remaining problems in choice of materials for BPP and cathode support that resist corrosion and provide low IR loss conduction	W-0.2 Cu is unsuitable without major work; CTE and resistance to oxidizing gases are favorable; it failed under cathodic polarization due to water in pores under Ag plate and local corrosion couples.
10a	0	Bipolar Plates	Not investigated	Choice of graphite sound, but air infiltration and sealing problems	Sealing problems, oxidation of exposed graphite	Material and source identified; Synthetic graphite chosen because of low IR loss and weight; Major problems in seal
10b	-	Bipolar seals on scale	Not investigated	Not addressable	Used Ni or SS plates instead of graphite.	Problem depends on BPP material; not addressable without materials choice

Status code: + Problems substantially solved or routes defined to solution;
0 Problems not addressed
- Major problems encountered and remain unsolved

.

2a. Separator Instability. An unanticipated problem was encountered in the physical stability of the separator. When exposure times of the cathode/separator assembly were sufficient to fully activate the cathode, both stand-alone and alpha1 separators were found to undergo a progressive loss conductivity (by an order of magnitude or more) which we attributed to a phase change and consequent disintegration. In one case, the full-scale separator underwent a disintegration upon thermal cycling accompanied by formation of triclinic phase. Samples of old (pre November 2004) and later deliveries were found to differ in relative amounts of tetragonal and cubic phases, with the latter deliveries showing an unstable mixture of cubic and tetragonal phases and a less-than-sufficient Y stabilization. We attribute loss of conductance to a tendency to disintegrate called "rubbleization." We have not found a remedy other than improved quality control in manufacturing and an increase in yttria concentration.

CEI has pointed out that in any case instability and disintegration of the separator cannot by itself account for the very low power of some current cell tests, and that methods of assembly (see discussion below on assembly techniques) may play the decisive role.

2b. Separator Wetting. An unknown at the start of the project was the ability of the fabric zirconia separator to retain sufficient molten salt by wetting to act as a gas impermeable membrane that isolates the anode from the cathode air. Post mortem visual examination of vertical separators of height 10 cm showed them to be fully melt-saturated. Operation under positive anode Ar overflow pressure in the anode chamber (without flooding and shutting off the cathode) supports the conclusion that the molten salt wetted fabric provides a barrier at hydrostatic heights of 10 cm. For example, in the alpha 1.3 experiment, Ar, air and CO_2 flows were 10, 10 and 2 ml/s, with the Ar overpressure set at 1.63" water; no anomalous loss of cathode potential was observed over the range of 0-840 mA, which would indicate bleed through from anode to cathode chamber.

3. Anode Current Collector. Nickel screen or Exmet and silver screen or Exmet current collectors were found to be suitable for large scale anode use. The nickel screen was somewhat brittle after exposure to the CO_2 atmosphere above the carbon particle bed, yet remained pliable within the carbon/salt phase. The cause is unknown, but appears the result from a local corrosion couple between the electrode above and below the surface. The unusually high sulfur content of the test carbon A3 (1.2% S) may contribute to spalling corrosion of the nickel current collector.

4. Bonding agents and seals. Significant success was also found with the selection and experience with ceramic bonding agents for sealing the separator to the alumina frame, and sealing the spacing between the air cathode channel and the enclosing alumina frame.

5. Cell Containment Material (Frames) Solid frames made of dense alumina were slip cast, cured and precision machined by CoorsTek, Inc. (Golden CO). While stability of dense alumina was expected, the delivered cells showed that frames of sufficient dimensional tolerances could be obtained at a reasonable cost. Cells from this source and also dense alumina tubes were not chemically or physically compromised during high temperature testing and thermal cycling.

6. Cathode/Separator/Anode Assembly. Problems were encountered with the CSA assembly which constitutes the galvanic cell. During heat up of the alpha 1 assemblies, the cathode precursor metal foam would sometimes detach from the air channel base and warp. The separator would undergo blistering during operation, likely the result of desorption of air from the components of the cell, or boiling off of water in the salt or absorbed in the zirconia. The oxidation of the nickel foam catalyst precursor also leads to volume changes and distortion. To some extent, we believe these effects may be countered using a spring-loaded anode current

collector, which makes use of thermal expansion differences between the confining alumina frame and the anode screen to maintain or increase pressure on the separator during heat up. This approach is the subject of a record of invention arising from the CRADA, which will disclose details.

7. Anode Particle Bed Properties. Significant success was also found with the operation of the anode particle bed. Our wedge-shaped cell design requires a pathway of low-electronic resistance between reaction layers near to the separator and the bipolar plate. The conductivity of melt wetted particle beds consisting of salt and acetylene black developed a conductivity of 0.4 ohm-cm at 750 °C—sufficiently high for an interelectrode ohmic drop of 40 mV across a 1 cm wide chamber at a current density of 0.1 A/cm^2. The measurement technique did not distinguish between electronic conductivity and electrolytic or "Faradaic" current. Since the electrolytic conductivity is comparable to this level, we conclude that the electronic conductivity is comparatively small to the total measured. Our work leaves unresolved the magnitude of the contacting IR drop across the bed/graphite-plate interface. Further work may be of benefit to distinguish between electrolytic and electronic conduction modes, using the technique of complex impedance spectroscopy.

8. Anode Bed Feed. Our wedge-shaped cell design requires that the melt-wetted particle bed be sufficiently fluid to conform to the shape of the cell, maintaining good contact with the separator and bipolar plate at all times. This was confirmed in the latter Alpha 1 experiments, where a well-defined and level interface between the top of the anode bed and the gas phase was found. The bed appeared free of major gas bubble inclusions as well. Until these experiments confirmed flow and conformation, no work had been done on this scale.

9. Cathode Air Channels. The technical approach defined at the design review, March 3, 2006, specified that the air cathode flow channel unit (that supports and collects current from the cathode catalyst layer) would have the same coefficient of thermal expansion as the alumina frame surrounding it. An alloy having this property was a tungsten bronze, W-0.2 Cu. Samples of W-Cu bronze were used in the AVLIS program at LLNL, and withstood high temperature corrosive environments when coated with a vapor deposit of gold. Our channels were electroplated with silver from an aqueous bath. Upon operation in an alpha 1.0 experiment, the silver coating peeled from the surface, and a rapid corrosion of the underlying metal in the presence of the molten salt took place with the silver providing a local cathodic site for oxygen reduction. The initial reaction might have been caused by trace amounts of water and electroplating salt absorbed in pores of the metal, although the supplier assured us that the composite alloy was free of pores. Samples of the unplated bronze were subject to corrosion studies by immersion in molten salt in air; little corrosion was observed other than formation of a black film. We had insufficient time in the schedule to seek an improved protective coating, and the bronze was abandoned for 304 stainless steel plates of higher coefficient of thermal expansion. These plates did not require seals or protective surface coatings, but relied on a crushable seal that could not be thermally cycled.

10a. Bipolar Plate Operation. Attempts to electroplate the synthetic graphite plate to prevent rapid air oxidation failed because of absorption of water into the pores, which was found to diffuse through the porous electroplated surface even at room temperature. A vapor deposit of gold was applied to a carefully backed-out graphite slab, but was not tested in the alpha scale. While graphite is an ideal material from the standpoint of corrosion in carbonate (it is ~ 10^4 times more stable than our reactive fuels), its use will be limited by effectiveness of isolation from air on the cathode side, and from carbon dioxide and Boudouard corrosion on the anode side.

10b. Bipolar plate sealing. The bipolar plate sealing and isolation from air were not investigated. Failures of separator and leaks elsewhere in the system focused our attention away from sealing or isolating the bipolar plate to the point where conclusive tests on conductivity could be undertaken.

Materials Failure; Tungsten Bronze. A major materials failure was found with the W-0.2Cu bronze channels used to support the cathode current collector and catalyst. W-0.2Cu was chosen early in the project because of the close match between its coefficient of thermal expansion and that of the alumina frame. The choice of this material was fixed in the March 3 design review—a few weeks after project start. The material has been used at LLNL in components subject to high temperature oxidative environments. The tungsten, being reactive in air, was protected by gold surface plates. We chose silver electroplates from commercial baths. Moisture from the plating process was apparently absorbed into the interior of the W-0.2Cu structure, causing rupture of the electroplated layer at high temperatures followed by rapid air oxidation of the tungsten component. Several improved electroplating techniques were suggested, but the time delay in seeking a solution to this problem mitigated in favor of replacing the W-0.2Cu parts with stainless steel and compensating for the large differential in CTE using crushable seals. The tungsten bronze channels are also very heavy, although weight was not a controlling consideration in the design of the alpha prototype as it would be in the ultimate beta prototypes.

Engineering design and fabrication of Plate and Frame Fuel Cell

The approach to an Alpha prototype makes use of the plate and frame design shown in Figure 1.3 and 1.4. Cell components were designed for containment within a robust and reusable dense alumina frame. The cells were connected to each other by means of a conductive, bipolar plate, which obviated removal of high currents from the cell and consequent voltage losses. Fully dimensioned engineering drawings of this design were delivered to CEI in June 2006. The design includes a thermally matched air distribution channel made of tungsten bronze, but can be modified for use of a stainless steel channel with thermal expansion accommodated by a viscous glass or crushable alumino-silicate cement seal.

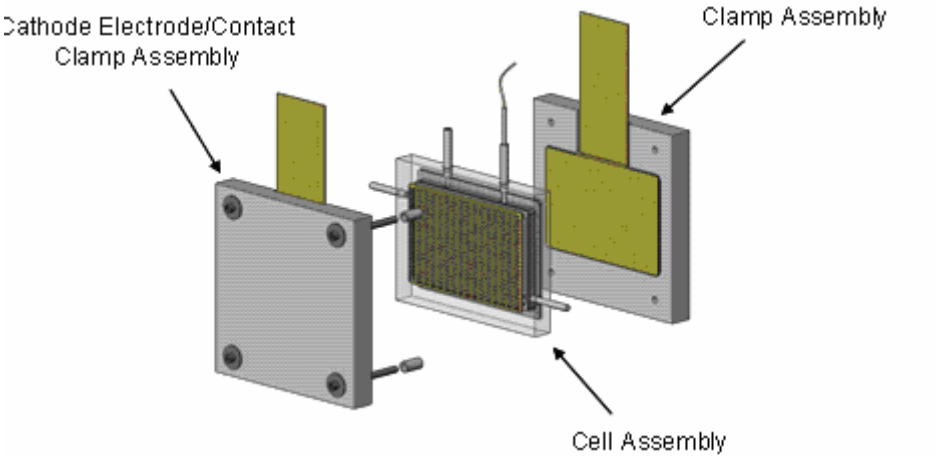

Figure 1.3. Basic plate and frame design of the fuel cell of active area 150 cm^2/cell. Up to five such cells may be contained within terminal bus clamps.

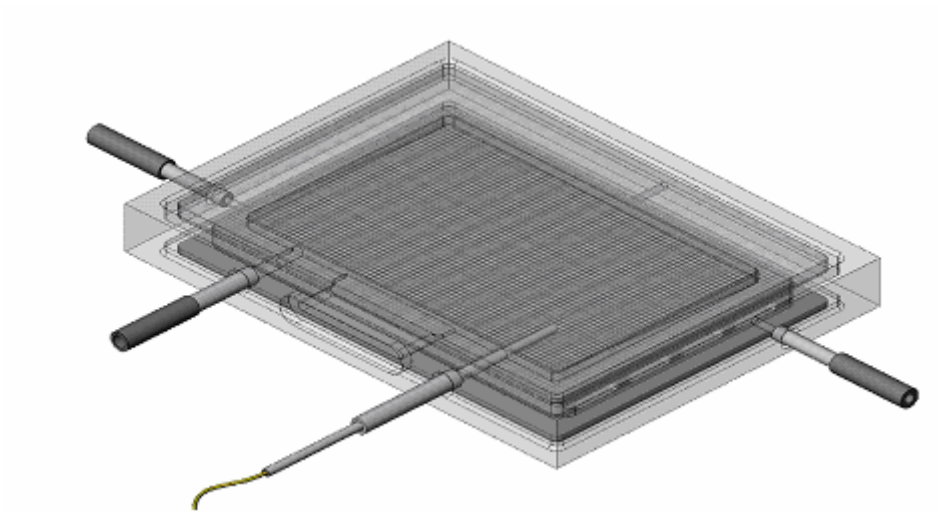

Figure 1.4. Detail of individual cell assembly is shown. The cell's top with fill port is to the left. Argon inflow and reference electrode probe are shown on either side of the fill port. The wedge graphite bipolar plate is indicated. Offset air entrance and exit tubes are shown left and right.

Choice of Reference Fuel.

We chose a manufactured carbon black, Arosperse 3 ("A3"), as a standard test material in view of high power density (70-100 mW/cm^2) reported for small cells at LLNL by Cherepy et al. (*J. Electrochem. Soc.* [2005]). We found we were not able to reproduce this power density with A3, achieving less than 40 mW/cm^2 even in cells of identical design. A special assembly technique and fixture (see below) is reported by CEI to improve results.

A3 has an unusually large concentration of sulfur (1.2%) compared with other materials tested. This level of sulfur promotes spalling corrosion of nickel and growth of an insulating nickel sulfide film on the surface of the nickel anode current collector. In retrospect, a more appropriate sulfur-free material would have been either acetylene black or commercial acid washed charcoal, both of which showed high power in tests reported in the same publication.

Assembly Techniques

At the time we finished our experimental work (March 15, 2007), we learned that Nerine Cherepy had used a special fixture to assemble cells, whereby the cathode/separator/anode current collector assembly (CSA) had been compressed by hand between two plastic cylinders of the same diameter as the CSA. In June, LLNL learned that CEI has reproduced the power level reported in 2005, after many experiments with this technique. The fixture has not been previously disclosed, but is apparently necessary to reproduce published results. CEI has also achieved power densities of up to 200 mW/cm^2 using specialty biochars.

The assembly technique in fixture may have increased contact area between the components of the CSA, by inter-digitation of anode screen, separator, and catalyst, reducing the tendency towards delaminating of the layers during heat up. Nonetheless, very high power densities (> 120 mW/cm^2) have been achieved for various materials including devolatilized coal (Cooper and Evans, 2004) without use of any special fixture. Still, CEI's suggestion is well taken—that much of what we were trying to ameliorate through improvement of separator stability, anode resistance, fuel wetting, and reference fuel choice may have been caused by loss of contact between adjacent components of the CSA during heat-up.

Mitigation of Technical Risk

All research and development entails technical risk. The requirement of placing engineering design and fabrication in parallel with testing and verification of components enhanced this risk, and lead to incomplete development of the desired prototype. Nonetheless, solution of a number of specific materials problems required for development Alpha prototype was achieved by LLNL under this CRADA, enabling CEI to move forward rapidly towards demonstrating the prototype. This process was speeded by CEI's success in implementing newly disclosed assembly techniques and biochar materials.

Invention Evolved From this CRADA

We observed during the first alpha tests that the separator tended to blister on the anode side, even though it maintained contact to the cathode elsewhere. To maintain contact between cathode catalyst, separator, and anode current collector in a large format (150 cm^2, 10 x 15 cm) cell, we proposed use of an anode screen convex to a congruent cathode support structure. The anode screen is confined by a rigid alumina plate of lower thermal expansion coefficient, while the cathode is unconstrained. As the temperature increases from ambient to working temperature, the enhanced thermal expansion of the confined screen increases the strain imposed on the separator, catalyst, and cathode support assembly, maintaining compression to counter a tendency for the assembly to warp and blister. The approach is inspired by the use of two parallel supporting heavy wires or Inconel in our small scale cells (April 2004, cleaned coal tests; see Figure 3.2 in Final Report for this CRADA), where pressure was assisted by the differential lengthening of the wires attached to anode screen, relative to the parallel confining alumina tube and cap. The invention is recorded as a Record of Invention in June 2007.

D. Expected Economic Impact

The ultimate use of this technology in the massive conversion of coal at efficiencies approaching 80% (based on carbon fraction) would have enormous impact on world-wide generation of electricity from coal (at a total efficiency of 30-35%). The increased efficiency (or reduction of greenhouse gas emissions) by a factor of two would extend the use of coal reserves by the same amount. One half of US electric power is generated by coal; China is deploying coal-fired power plants last year at the rate of 1 GW per day. In the words of former Laboratory Director Bruce Tarter, following a formal review of the technology in April 2004, successful demonstration of an efficient carbon fuel cell technology using coal would be valued in the billions of dollars.

D.1 Specific Benefits

Benefits to DOE

This CRADA project benefits DOE's mission to advance the efficiency of fossil fuel conversion to electric power, by providing the core of a disruptive technology to double the electric energy yield of coal without increased emissions. It also benefits DOE's mission to develop energy storage devices of very high energy density. This fuel battery is estimated to have an energy density of 2-4 kWh/kg—which is a factor of 10 times greater than today's lithium ion batteries.

Benefits to Industry

The proposed research demonstrates a fuel cell that converts elemental carbon derived from fossil fuels such as coal or petroleum coke at extraordinary efficiencies (up to 80% Higher Heating Value), 80% is the peak value of carbon we would like to obtain.

E. Partner Contribution

CEI actively participated in the project by review of the engineering designs beginning in March 2005; by purchase and delivery to LLNL of critical materials including cell alumina frames, cements, silver and nickel conductors, and a large kiln furnace. A computer was also provided which, together with automated data acquisition system, could be use in routine testing of Alpha level prototypes.

CEI conducted parallel research in cell performance, investigating novel means of maintenance of cell assembly during operation, and selecting and procuring sulfur-free standard anode test materials such as willow charcoal.

F. Documents/Reference List

Reports and presentations

1. Kevin Berner and John F. Cooper, Contained Energy, presentation to EPRI Direct Carbon Workshop, August 29, 2006, UCRL-PRES-225154, August 2007.
2. John F. Cooper, Mark Evans and Jeff Haslam, *Final Report: Research and Development of a Carbon Fuel Cell* (undergoing clear and release as an Official Use Only document; IM # 349018; June 18, 2007).

Copyright Activity

Detailed engineering drawings, including dimensions and specified materials, were produced by LLNL and delivered to Kevin Berner of Contained Energy, Inc., Cleveland. No copyright protection has been sought. The drawings are in the custody of CEI, Cleveland OH.

Subject Inventions

IL-11873, Patent being pursued

Background Intellectual Property

LLNL disclosed the following Background Intellectual Property for this project:

IL-11331, Patent pending

IL-11132, Patent not pursued

IL-10847, Patent pending

IL-10917, Patent pending

IL-11101, Patent pending

IL-11234, Patent pending

IL-11267, Patent pending

U.S. Patent No. 6,815,105 (LLNL Docket IL-10479) - *Fuel Cell Apparatus and Method Thereof*; Issued 11/09/04; Inventors: John F. Cooper, Roger L. Krueger, Nerine J. Cherepy

U.S. Patent No. 6,878,479 (LLNL Docket IL-10848) - *Tilted Fuel Cell Apparatus*; Issued 04/12/05; Inventors: John F. Cooper, Roger L. Krueger, Nerine J. Cherepy

Contained Energy licensed the above Background Intellectual Property under LLNL License Agreement No. TL01955-0.0, executed on September 23, 2005.

Contained Energy, Inc. did not disclose any Background Intellectual Property for this project.

G. Acknowledgement

Industrial Participant's signature of the final report indicates the following:

1) The Participant has reviewed the final report and concurs with the statements made therein.
2) The Participant agrees that any modifications or changes from the initial proposal were discussed and agreed to during the term of the project.
3) The Participant certifies that all reports either completed or in process are listed and all subject inventions and the associated intellectual property protection measures generated by his/her respective company and attributable to the project have been disclosed and included in Section E or are included on a list attached to this report.
4) The Participant certifies that if tangible personal property was exchanged during the agreement, all has either been returned to the initial custodian or transferred permanently.
5) The Participant certifies that proprietary information has been returned or destroyed by LLNL.

6/27/2007

J. Kevin Berner, CEO
Contained Energy, Inc.

Date

6/28/2007

John F. Cooper, LLNL Principal Investigator
Lawrence Livermore National Laboratory

Date

6/28/07

Karena D. McKinley, IPAC Director
Lawrence Livermore National Laboratory

Date

Attachment I – Final Abstract

Development and Demonstration of Carbon Fuel Cell

Final Abstract (Attachment I)
CRADA No. TC02091.0
Date Technical Work Ended: April 30, 2007

Date: June 24, 2007 Revision: 2

A. Parties

This project was a relationship between Lawrence Livermore National Laboratory (LLNL) and Contained Energy, Inc. (CEI).

The Regents of the University of California
Lawrence Livermore National Laboratory
7000 East Avenue
Livermore, CA 94550
John F. Cooper
Tel: (925) 423-6649
Fax: (925) 422-6892

Contained Energy, Inc.
2980 Fontenay Road
Shaker Heights, OH 44120
J. Kevin Berner
Tel: (216) 973-1762
Fax: (216) 283-5148

B. Purpose and Description

This was a collaborative effort between The Regents of the University of California, Lawrence Livermore National Laboratory (LLNL) and Contained Energy, Inc. (CEI), to conduct necessary research and to develop, fabricate and test a multi-cell carbon fuel cell.

The work proposed under this CRADA is intended to resolve issues concerning the air cathode structure and support, separator wetting with molten salt, and gravity feed of the anode material within sealed cells. Success in developments early in the project will allow construction of a multi-cell stack comprised of five cells in bipolar series connection with operation as a fuel battery.

We intended to demonstrate the discharge of a five-cell stack with bipolar construction as the major accomplishment of the project, with demonstration of operation for a period of 100 hours. This demonstration was not achieved because of unforeseen problems in the stability of the zirconia fabric separator and of a tungsten-copper bronze air channel designed to match the thermal properties of dense alumina frame. These problems prevented successful assembly of the

Alpha 1 single cell that was prerequisite to proceeding to a 5-cell Alpha 2 prototype including bipolar series connection plates to be developed at that stage.

Nonetheless significant technical successes were achieved in critical technologies: (1) a technique of in situ formation and activation of lithiated nickel oxide catalyst was researched and successfully developed, matching electrical properties reported in literature; (2) a low-cost, high tolerance alumina frame design was developed and procured for tests here and subsequently at CEI; (3) by examination of separators following large cell discharge, the baseline yttria-stabilized zirconia (YSZ) separator was found to maintain wetting over hydrostatic heads of at least 10 cm—a prerequisite for the cell designs of the alpha 2 modules; (4) the ability of the carbon particle bed (saturated with molten salt) to fall under its own weight and conform to the interior geometry of the anode chamber of the alpha 2 design was shown experimentally; (5) sufficient conductance (0.4 Ω-cm) of the carbon anode bed (for high conductivity anode fuels) was shown for dimensions comparable to anode bed thickness with voltage drops of 40 mV at 100 mA/cm^2.

These and other problems encountered and/or solved by the CRADA are summarized in Table 1.2 in the extended report. One invention evolved from the CRADA, providing a method and configuration for continuously maintaining compressive loading of cell components while the cell is undergoing initial heat-up.

In all, successful development of a 5-cell alpha 2 prototype required success in all of 12 major technical challenges that were identified prior to the CRADA. We were able to achieve success (or identify a clear route to same) in 10 of the 12 problems, yet progress towards the Alpha 2 demonstrations was curtailed because of separator and air channel instability. Nonetheless, solution of most of the specific materials problems required for development Alpha prototype was achieved by LLNL under this CRADA, enabling CEI to move forward rapidly to demonstrate the prototype.

C. Benefit to Industry

The proposed research demonstrates a fuel cell that converts elemental carbon derived from fossil fuels such as coal or petroleum coke, to electricity at extraordinary efficiencies (up to 80% higher heating value of carbon).

D. Benefit to DOE/LLNL

This CRADA project benefits DOE's mission to advance the efficiency of fossil fuel conversion to electric power, by providing the core of a disruptive technology to nearly double the electric energy yield of coal without increased emissions. It also benefits DOE's mission to develop energy storage devices of very high energy density. This fuel battery is estimated to have an energy density of 2-4 kWh/kg—which is a factor of 10 times greater than today's lithium ion batteries.

E. Project Dates

January 18, 2006 through April 30, 2007