LAWRENCE LIVERMORE NATIONAL LABORATORY

LLNL-TR-739171

Research and Development of Zinc Air Fuel Cell To Achieve Commercialization Final Report CRADA No. TC-1544-98

J. F. Cooper, H. D. Haley

September 29, 2017

Disclaimer

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

Research and Development of Zinc Air Fuel Cell To Achieve Commercialization

Final Report
CRADA No. TC-1544-98
Date Technical Work Ended: December 2002

Date: November 24, 2003 Revision: 1

A. Parties

This project was a relationship between Lawrence Livermore National Laboratory (LLNL) and Power Air Tech, Inc.

The Regents of the University of California
Lawrence Livermore National Laboratory
7000 East Avenue
Livermore, CA 94550
John F. Cooper, Principal Investigator
Tel: (925) 423-6649
Fax: (925) 422-0049

Power Air Tech, Inc.
3801 Albert Matthews Road
Columbia, TN 38401
H. Dean Haley
Tel: (931) 388-4891
Fax: (931) 388-3627

B. Project Scope

The specific goal of this project was to advance the development of the zinc air fuel cell (ZAFC) towards commercial readiness in different mobile applications, including motor bikes, passenger cars, vans, buses and off-road vehicles (golf carts, factory equipment), and different stationary applications including generator sets, uninterruptible power systems and electric utility loading leveling and distributive power.

This original Statement of Work (SOW) for this project consisted of three major tasks and subtasks:

Task 1 – Research and Development (LLNL and PAT, Inc.)
1.1 – Component Development
1.2 – Module Development
1.3 – Process Development

Task 2 – Bench Top ZAFC/ZRU Demonstration (LLNL & PAT, Inc.)

Task 3 – Bench Top Quarter Scale Demonstration (LLNL & PAT, Inc.)

Amendment One, executed on August 9, 2000, extended the CRADA for an additional seven months, and modified the SOW by deleting Tasks 2 and 3 above and replacing them with the following tasks:

Task 2 – Develop and demonstrate a Prototype 6-cell (1/4 kW and 2 kWh) zinc air fuel cell module

Task 3 – Evaluate and select air electrodes

Task 4 – Optimize "current collection" Technology

Task 5 – Verify operation of separators

Deliverables:
An engineering prototype 6-cell (1/4 kW peak and 2 kWh nameplate) zinc/air fuel cell stack.

Test results and design drawings to be delivered to PAT, Inc. for design for manufacture for a variety of commercial stationary and mobile power applications.

Amendment Two, executed on 3/6/01, increased the funds-in amount.
Amendment Three, executed 4/11/01, added funds, tasks and deliverables and extended the CRADA to 5/31/01. The following two tasks and deliverables were added to the SOW:

Task 6 – Construct and Test Three 6-Cell Stacks
Task 7 – Scope Engineering Approach to Near-Term Emergency Power Pack (EPP)

Deliverables:
Task 6: Three 6-cell stacks will be constructed and tested. Two will be new and one will be refurbished from existing hardware.

Task 7: An approach to an emergency power supply will be outlined, including sketches for a replaceable bipolar electrode cassette.

Amendment 4 extended CRADA to 9/30/01 and added the following tasks and deliverables:

Task 8 – Design, draft, fabricate, and test one 12-cell stack
Task 9 – Fabricate and test three 12-cell modules

Deliverables:
Task 8: Design and fabricated one (1) 12-cell stack (split electrolyte flow and parallel air flow), documented by Pro-E design drawings. (LLNL)

Discharge tests at constant cell current (60 A) for thirty (30) hours. (LLNL)

Cell will be constructed of polysulfone plate (or equivalent) and cemented together with permanent bonding agent (such as epoxy). (LLNL)

Cell will demonstrate a sustained rated power of 600 watts. (LLNL)

Task 9: Fabricate and test three 12-cell modules (LLNL and PAT, Inc.)

Amendment 5 added funds-in required to complete tasks and extended CRADA to 2/28/02.

The research effort was completed within the specified time duration.

C. Technical Accomplishments

The technical accomplishments are given below, in reference to each task.

Task 1 – Research and Development
1.1 – Component Development

We developed and tested specific components as follows: advanced current collection techniques were developed allowing more efficient feed through of current through the bipolar plate. The gap dimensions in the conduit connecting hopper to cell was increased to its limit and roughness minimized to prevent holdup of the particulate zinc fuel; a special weir was developed and emplaced to prevent leakage of zinc into the return path; a serious design error at the electrolyte inlet was corrected. These components were assembled in single cells and successful verified by test.

1.2 – Module Development

Modules, or self-standing assemblies of 3-6 cells, were developed successfully and integrated with an internal electrolyte and airflow subsystem. Advanced sealing techniques involving strong-backs were developed and tested. Modules from this work were assembled and discharged at Argonne National Laboratory USABC Battery testing facility (the tests were financed by DOE) and met or exceeded all specs and previous results. Tests included peak sustainable power; peak power a successive stages of discharge, and performance as functions of temperature.

1.3 – Process Development

Process development (originally intended to include zinc recycling from battery reaction product) was scaled back to provide time/funds to address more immediate problems in processes. These problems included: method of heat up of the electrolyte upon startup (addressed through thermal modeling and incorporating a closed loop design intended to conserve heat); a flow-over technique for preventing the possibly hazardous accumulation of hydrogen gas in the hoppers; and analyses of shut-down losses. A major effort of modeling of various process options (i.e., scale of fuel cell, method of recycling, and quantitative estimates of size and cost) replaced laboratory experimentation in zinc electroplating from battery products and pellet formation mechanics. Our CRADA partner encouraged these changes, and we agreed.

Task 2 – Develop and demonstrate a Prototype 6-cell (1/4 kW and 2 kWh) zinc air fuel cell module

This task was successfully pursued although the power levels demonstrated exceeded specifications. A prototype 6-cell was developed and tested (as part of module tests, task 1.2) and showed power levels to 380 W (exceeded expectations of 250 W). The 2 kWh scale (in a fuel cell, merely the quantity of electrolyte and zinc present in the system) was reduced to meet particulars of the USABC Testing profiles. In all, all performance expectations were met or exceeded.

Task 3 – Evaluate and select air electrodes

This task was cut back, as the number of commercially available air electrodes was greatly reduced during this work period as several suppliers went out of business. We did evaluate and select the AET air electrode that proved sufficiently robust for extended tests (and repeated tests) but we have no life data on the air electrode at all.

Task 4 – Optimize "current collection" Technology

We improved current collection techniques and measured these improvements by direct measurement of IR drop between the two faces of the bipolar plate that connects anode to cathode. This involved improved feed-through disks.

Task 5 – Verify operation of separators

This task was obviated by the procurement of improved separators that operated without failure.

Task 6 – Construct and Test Three 6-Cell Stacks

At least three 6-cell stacks were designed, constructed and tested, for data that they yielded and also for demonstrations to prospective CRADA customers.

Task 7 – Scope Engineering Approach to Near-Term Emergency Power Pack (EPP)

An engineering approach to a near-term power pack was designed on paper and a cardboard model was constructed. The key element of this design is a modular cell built out of stamped plastic sheets, and assembled and held together by pressure applied to either end of the stack. This allows individual cells to be removed and replaced upon dysfunction or failure. This is a difficult task, and was only scoped, as it meant matching flow channels from adjacent cells using nothing but stamped plastic sheets.

Task 8 – Design, draft, fabricate, and test one 12-cell stack

We designed, drafted, and fabricated sufficient parts for one 12-cell stack. Actual testing was postponed until after the CRADA term and completed off-site as part of a demonstration. We elected to join two separate 6-cell stacks in parallel plumbing to increase probability of success and allow individual modules to be remove/replaced upon failure or dysfunction.

Task 9 – Fabricate and test three 12-cell modules

> This work was not completed by this CRADA due to insufficient funds and time to test. Nevertheless the results of task 8 far exceeded any performance achievements at any time in the past. The design perfected in task 8 allows our CRADA partner to separately pursue fabrication and tests of any number of 12-cell modules.

The deliverables, and our successes in meeting them, are described below:

Deliverables:
An engineering prototype 6-cell (1/4 kW peak and 2 kWh nameplate) zinc/air fuel cell stack:

All deliverables achieved or exceeded.

Test results and design drawings to be delivered to PAT, Inc. for design for manufacture for a variety of commercial stationary and mobile power applications.

This was accomplished

Three 6-cell stacks will be constructed and tested. Two will be new and one will be refurbished from existing hardware.

This was accomplished

An approach to an emergency power supply will be outlined, including sketches for a replaceable bipolar electrode cassette.

This was accomplished

Design and fabricated one (1) 12-cell stack (split electrolyte flow and parallel air flow), documented by Pro-E design drawings

Discharge tests at constant cell current (60 A) for thirty (30) hours.

Cell will be constructed of polysulfone plate (or equivalent) and cemented together with permanent bonding agent (such as epoxy).

Cell will demonstrate a sustained rated power of 600 watts

Fabricate and test three 12-cell modules

We designed 6 6-cell modules but tested three of them singly; 12-cell module test was *completed after term of CRADA by PAT, Inc.*

In summary, tasks 1 through 7 were successfully completed; task 8 was completed with revision of goals; and task 9 could not be fully completed due to unexpected technical difficulties and cost of obtaining cell hardware and air electrodes.

With the exception of the last task, the research effort was completed within the specified time duration.

D. Expected Economic Impact

Given successful implementation of this technology, the economic impact on the US comes primarily from the manufacture of the critical elements of the zinc/air fuel cell. These elements include the air electrode and its housing called the air cathode module. This unit comprises the "new and unique" aspect of the technology, and the CRADA partner has agreed to the manufacture of this in the US. The economic impact of the production of ten million fuel cell units of power rating 50 W per cell can be estimated from the unit cost per kW and the assumption of a nominal (i.e., 15%) markup and the manufacturing cost markup of 20%. Given $100/kWh cost targets for materials used in the fuel cell stack, manufacturing cost would be $50,000,000; profit markup would be 7.5 $M; manufacturing cost would be 10 $M. These figures are crude estimates, as the accurate determination of manufacturing cost was beyond the scope of the project.

D.1 Specific Benefits

Benefits to DOE:
This CRADA supports DOE's mission to foster a secure and reliable energy system that is environmentally and economically sustainable. More specifically, it supports DOE/EE's mission to promote the research, development, and private sector application of cost-effective transportation and industrial technologies and practices that support sustainable production and use of energy. This project develops technologies capable of improving energy conversion efficiency and limiting U.S. dependence on foreign energy resources and reducing pollution.

The proposed zinc air fuel cell developed is also applicable/consistent to DOE/EE's Heavy Vehicle program and current thrusts in energy storage and propulsion technology developments such as US Advanced Battery Consortium, Fuel Cell Program, and the Partnership for a New Generation of Vehicles (PNGV) Presidential Initiative. Zinc air is consistent with the US Advanced Battery Consortium goals and could be used to meet the goals of the post-PNGV Program.

LLNL's collaboration with PAT, Inc. would allow us to realize the potential of this investment, insight and taxpayer's money to the benefit of the U.S. and the world. The experience gained by LLNL scientists will be applied to current and future DOE programs.

Benefits to Industry:

This CRADA will enable industry to bring the zinc air technology to the point that prototype fuel cells can be fabricated. The electrochemistry and technical nuisances of fabrication with existing air electrodes were developed by LLNL and transferred to PAT, Inc. Other companies will be spurred to develop technologies to compete with zinc air thus improving fuel cell availability and performance.

E. Partner Contribution

The industrial partner focused our technical efforts on the markets of particular interest. These included (1) electric propulsion for small, urban busses on circuits requiring frequent stops and requiring only low power (low speeds, flat terrain). (2) Small (0.5-1 kW) electric power sources for mopeds and lightweight motor scooters, intended for urban markets abroad. (3) 1-5 kW scale transportable power sources ("gen sets") intended for use at construction sites or for emergency use. The partner defined specifications of performance, suggested technical adaptations for these markets, and obtained detailed operating and environmental conditions necessary for focusing the technology. The partner made accurate determinations of the scope and prospects for foreign markets for the fuel cells that the partner would manufacture in the US.

There were no subject inventions made during the course of this CRADA by PAT, Inc.

F. Documents/Reference List

Reports

1. John F. Cooper, Nerine Cherepy, Roger Krueger and Frank Tokarz, "The LLNL Zinc/Air Fuel Cell Design, Development, and Testing for Commercialization in Stationary and Mobile Power Applications," Lawrence Livermore National Laboratory Report UCRL-ID-140427 August 7, 2000
2. Performance of the Zinc/Air Refuelable Battery from Lawrence Livermore National Laboratory, (I. Bloom and E. G. Polzin, Electrochemical Technology Program Argonne National Laboratory. Prepared for the U.S. Department of Energy Office of Heavy Vehicle Technologies; April 2001).

Copyright Activity

None

Subject Inventions

No subject inventions were made during the course of this CRADA. Significant, but not patentable improvements were made to design particulars. Information proprietary to PAT Inc. was developed.

Background Intellectual Property

LLNL disclosed the following Background Intellectual Property (BIP) for this project:

U.S. Patent No. 5,578,183, (LLNL Docket IL-9407) - *Production of Zinc Pellets*; issued 11/26/96; Inventor: John F. Cooper

U.S. Patent No. 5,434,020, (LLNL Docket IL-8776) - *Continuous-Feed Electrochemical Cell with Non-Packing Particulate Electrode*; issued 7/18/95; Inventor: John F. Cooper

Power Air Tech. Inc. executed a Limited Exclusive License for the above LLNL BIP on March 31, 2001.

Pat, Inc., declared no BIP for this project.

G. Acknowledgement

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.

H. Dean Haley, CEO — Date
Power Air Tech. Inc.

J. Ray Smith, Advanced Energy Technology Program Leader — Date
Lawrence Livermore National Laboratory

1/6/04

Karena D. McKinley, IPAC Director — Date
Lawrence Livermore National Laboratory

Attachment I – Final Abstract

Research and Development of Zinc Air Fuel Cell to Achieve Commercialization

Final Abstract (Attachment I)
CRADA No. TC-1544-98
Date Technical Work Ended: December 15, 2001

Date: November 24. 2003 Revision: 1

A. Parties

This project was a relationship between Lawrence Livermore National Laboratory (LLNL) and Power Air Tech, Inc.

The Regents of the University of California
Lawrence Livermore National Laboratory
7000 East Avenue
Livermore, CA 94550
John F. Cooper, Principal Investigator
Tel: (925) 423-6649
Fax: (925) 422-0049

Power Air Tech, Inc.
3801 Albert Matthews Road
Columbia, TN 38401
H. Dean Haley
Tel: (931) 388-4891
Fax: (931) 388-3627

B. Purpose and Description

The specific goal of this project was to advance the development of the zinc air fuel cell (ZAFC) towards commercial readiness in different mobile applications, including motor bikes, passenger cars, vans, buses and off-road vehicles (golf carts, factory equipment), and different stationary applications including generator sets, uninterruptible power systems and electric utility loading leveling and distributive power.

This original Statement of Work (SOW) for this project consisted of three major tasks. There were a total of five amendments to the CRADA, which expanded the scope of work and deliverables for the project, and extended the term of the CRADA. The following tasks and deliverables were to be completed for this project. Under each task heading, the status is described as of close of CRADA work (December 15, 2001).

Task 1 – Research and Development

1.1 – Component Development

We developed and tested specific components as follows: advanced current collection techniques were developed allowing more efficient feedthrough of current through the bipolar plate. The gap dimensions in the conduit connecting hopper to cell was increased to its limit and roughness minimized to prevent holdup of the particulate zinc fuel; a special weir was developed and emplaced to prevent leakage of zinc into the return path; a serious design error at the electrolyte inlet was corrected. These components were assembled in single cells and successful verified by test.

1.2 – Module Development

Modules, or self-standing assemblies of 3-6 cells, were developed successfully and integrated with an internal electrolyte and airflow subsystem. Advanced sealing techniques involving strong-backs were developed and tested. Modules from this work were assembled and discharged at Argonne National Laboratory USABC Battery testing facility (the tests were financed by DOE) and met or exceeded all specs and previous results. Tests included peak sustainable power; peak power a successive stages of discharge, and performance as functions of temperature.

1.3 – Process Development

Process development (originally intended to include zinc recycling from battery reaction product) was scaled back to provide time/funds to address more immediate problems in processes. These problems included: method of heat up of the electrolyte upon startup (addressed through thermal modeling and incorporating a closed loop design intended to conserve heat); a flow-over technique for preventing the possibly hazardous accumulation of hydrogen gas in the hoppers; and analyses of shut-down losses. A major effort of modeling of various process options (i.e., scale of fuel cell, method of recycling, and quantitative estimates of size and cost) replaced laboratory experimentation in zinc electroplating from battery products and pellet formation mechanics. Our CRADA partner encouraged these changes, and we agreed.

Task 2 – Develop and demonstrate a Prototype 6-cell (1/4 kW and 2 kWh) zinc air fuel cell module

This task was successfully pursued although the power levels demonstrated exceeded specifications. A prototype 6-cell was developed and tested (as part of module tests, task 1.2) and showed power levels to 380 W (exceeded expectations of 250 W). The 2 kWh scale (in a fuel cell, merely the quantity of electrolyte and zinc present in the system) was reduced to meet particulars of the USABC Testing profiles. In all, all performance expectations were met or exceeded.

Task 3 – Evaluate and select air electrodes

This task was cut back, as the number of commercially available air electrodes was greatly reduced during this work period as several suppliers went out of business. We did evaluate and select the AET air electrode that proved sufficiently robust for extended tests (and repeated tests) but we have no life data on the air electrode at all.

Task 4 – Optimize "current collection" Technology

We improved current collection techniques and measured these improvements by direct measurement of IR drop between the two faces of the bipolar plate that connects anode to cathode. This involved improved feed-through disks.

Task 5 – Verify operation of separators

This task was obviated by the procurement of improved separators that operated without failure.

Task 6 – Construct and Test Three 6-Cell Stacks

At least three 6-cell stacks were designed, constructed and tested, for data that they yielded and also for demonstrations to prospective CRADA customers.

Task 7 – Scope Engineering Approach to Near-Term Emergency Power Pack (EPP)

An engineering approach to a near-term power pack was designed on paper and a cardboard model was constructed. The key element of this design is a modular cell built out of stamped plastic sheets, and assembled and held together by pressure applied to either end of the stack. This allows individual cells to be removed and replaced upon dysfunction or failure. This is a difficult task, and was only scoped, as it meant matching flow channels from adjacent cells using nothing but stamped plastic sheets.

Task 8 – Design, draft, fabricate, and test one 12-cell stack

We designed, drafted, and fabricated sufficient parts for one 12-cell stack. Actual testing was postponed until after the CRADA term and completed off-site as part of a demonstration. We elected to join two separate 6-cell stacks in parallel plumbing to increase probability of success and allow individual modules to be remove/replaced upon failure or dysfunction.

Task 9 – Fabricate and test three 12-cell modules

This work was not completed by this CRADA due to insufficient funds and time to test. Nevertheless the results of task 8 far exceeded any performance achievements at any time in the past. The design perfected in task 8 allows our CRADA partner to separately pursue fabrication and tests of any number of 12-cell modules.

Deliverables:

An engineering prototype 6-cell (1/4 kW peak and 2 kWh nameplate) zinc/air fuel cell stack:

All deliverables achieved or exceeded.

Test results and design drawings to be delivered to PAT, Inc. for design for manufacture for a variety of commercial stationary and mobile power applications.

This was accomplished

Three 6-cell stacks will be constructed and tested. Two will be new and one will be refurbished from existing hardware.

This was accomplished

An approach to an emergency power supply will be outlined, including sketches for a replaceable bipolar electrode cassette.

This was accomplished

Design and fabricated one (1) 12-cell stack (split electrolyte flow and parallel air flow), documented by Pro-E design drawings

Discharge tests at constant cell current (60 A) for thirty (30) hours.

Cell will be constructed of polysulfone plate (or equivalent) and cemented together with permanent bonding agent (such as epoxy).

Cell will demonstrate a sustained rated power of 600 watts

Fabricate and test three 12-cell modules

We designed 6 6-cell modules but tested three of them singly; 12-cell module test was completed after term of CRADA by PAT, Inc.

Tasks 1 through 7 were successfully completed; task 8 was completed with revision of goals; and task 9 could not be fully completed due to unexpected technical difficulties and cost of obtaining cell hardware and air electrodes.

The research effort was completed within the specified time duration.

C. Benefit to Industry

This CRADA will enable industry to bring the zinc air technology to the point that prototype fuel cells can be fabricated. The electrochemistry and technical nuisances of fabrication with existing air electrodes were developed by LLNL and transferred to PAT, Inc. Other companies will be spurred to develop technologies to compete with zinc air thus improving fuel cell availability and performance.

D. Benefit To DOE/LLNL

This CRADA supports DOE's mission to foster a secure and reliable energy system that is environmentally and economically sustainable. More specifically, it supports DOE/EE's mission to promote the research, development, and private sector application of cost-effective transportation and industrial technologies and practices that support sustainable production and use of energy. This project develops technologies capable of improving energy conversion efficiency and limiting U.S. dependence on foreign energy resources and reducing pollution.

The proposed zinc air fuel cell developed is also applicable/consistent to DOE/EE's Heavy Vehicle program and current thrusts in energy storage and propulsion technology developments such as US Advanced Battery Consortium, Fuel Cell Program, and the Partnership for a New Generation of Vehicles (PNGV) Presidential Initiative. Zinc air is consistent with the US Advanced Battery Consortium goals and could be used to meet the goals of the post-PNGV Program.

LLNL's collaboration with PAT, Inc. would allow us to realize the potential of this investment, insight and taxpayer's money to the benefit of the U.S. and the world. The experience gained by LLNL scientists will be applied to current and future DOE programs.

E. Project Dates

December 11, 1998 to December 15, 2001