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13. ABSTRACT (Maximum 200 words) This program investigated the fundamental limiting factors associated with thermophotovoltaic energy conversion and the phenomenon associated with unique composite electrodes for use in batteries, capacitors, and fuel cells. In the TPV project, emittance, efficiency, and strength have been characterized. TPV mantles have been fabricated and tested to 1700 k. Uniformity of emission has been demonstrated. A "Benchtop" system was constructed and evaluated. A detailed model is working and has been reported in the literature. The model has been modified to make it easier to use. A vapor pressure facility has been constructed and is operational. Several samples have been fabricated for other Army contractors. PEM membrane-electrode assemblies have been developed with platinum-catalyzed, activated nickel composite fiber electrodes. Electrodes have been built for lithium-ion batteries. Electrodes have been built for electrochemical capacitors using double layer and pseudo capacitors as the storage mechanism.				
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MOBILE BATTLEFIELD POWER TECHNOLOGY

FINAL REPORT

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U. S. ARMY RESEARCH OFFICE

DAAL03-92-G-0205

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INTRODUCTION

This University Research Initiative, URI, was funded in 1992 at a time when it was just being realized that major changes in the way the military provides energy to soldiers in the field could be, and needed to be, changed. Since that time, technology has drastically altered the nature of armed conflict. The success of Desert Storm and the "lessons learned" point clearly to the advantages of smart ordnance, information dominance, and speed. The battlefield is now highly complex due to the capabilities and sensory inputs available to inflict damage to an enemy. The Army must now be highly mobile and have a specialized force structure capable of rapid deployment in order to effectively use the ever increasing set of "smart" ordnance, information, and equipment. The world technical community is highly integrated. Technology purchased from a local electronic supply house can give a soldier capability far superior to that used in WW II. The future Army could be faced with a threat consisting of smart technologies on par with our own, or even manufactured within our military industrial infrastructure.

The amazing array of capabilities available to the military comes with a price. The increased technological sophistication levies higher burdens on the energy sources available to power the devices. The most pressing questions to the military are battery type, fuel type, autonomy time needed, absolute power, reliability, commonality, cost, etc. These are the factors that will impact the shape of the battlefield as much as, if not more than, the capability available from technological advances in communications, computing, sensing, lethality of weapons, and protection. It is highly probable that the individual soldier may have to function in a biological, chemical or nuclear environment. Comfortable protective clothing will be necessary to protect the most important aspect of the system - the human body. The works performed within this URI and the Prospector Series of Workshops have made important contributions to the technologies necessary to provide new energy sources within a battlefield environment. They have also contributed to the slow paradigm shift that has brought the military to the point of accepting new ways to provide energy for the dismounted forces. There have been numerous studies which have clearly recognized the need for major advances in power technology within the framework of future battlefield scenarios.(1,2,3,4,5) Each new application must have the ultimate in energy storage density if it is to be truly revolutionary for the military. Anything less results in a loss of capability or an increased logistics burden due to the increase in re-supply intervals.

The basic types of energy systems within the inventory have not changed appreciably since WW II. The motor-generator and the battery are still the primary energy sources for the dismounted soldier. These technologies are now mature. Technologies that long in service have been improved to the point where only incremental changes in desirable parameters appear possible. The specific energy of batteries are approaching or exceeding that of explosives. Safety becomes an issue both from the perspective of storage and usage. Everything that the Dismounted Soldier takes into the field must be

compact and rugged. Issues such as availability of fuel, specific energy, specific power, minimal signature (thermal, chemical, and acoustic), orientation-independence, ruggedization, simplicity of operation, and reliability are of great concern. These limiting factors translate to materials as critical research issues since the limits placed on the materials directly determine operational limits. The mass that a soldier must carry to combat is approaching the limits of the average soldiers' ability. It is sometimes necessary to trade-off bullets or food for energy sources to power the soldier's electronic/sensor ensemble.

Advanced energy source technology is multi-disciplinary. The ultimate utility of a particular technology may not reside in the engineering of the device itself but in the electrode technology or in the availability of the fuel needed to power it. Any reduction in energy demand for the same capability translates into increased mission time for the same mass or the same mission with reduced mass. Available fueled systems, in general, are low in specific energy except for long run times where fuel mass dominates the system mass and low in specific power for the same reasons. Scaling to small sizes is only now being understood. Recent advances in "fueled" technologies as **PEM fuel cells, thermophotovoltaics, Alkali Metal Thermal to Electrical Converters (AMTEC), and microturbines** appear capable of producing higher specific energy and specific power than fueled systems currently employed in the form of motor-generator sets. These technologies appear to scale favorably to small sizes. Fieldable technology rarely equals laboratory prototype or theoretical capability. Obstacles sometimes are fundamental and perhaps can be finessed through appropriate R&D, innovative techniques, and skillful engineering. The power level of a fueled system is determined by the converter design. The specific power decreases with the addition of fuel. This is direct contrast to batteries where the specific power stays constant.

The topics researched within this URI contributed significantly to the technology base, which is currently evolving to practical options for energy sources for the Dismounted Soldier. As time progressed, tasks were added or deleted to make the URI more responsive to the Army's needs. The tasks researched within this URI are:

Task I Thermophotovoltaic Energy Conversion

Task II Composite Fiber Electrode Structures for Chemical Energy Storage and Production

Task III Electrical Characterization of Exploding Liquid Metal Jets

Task IV Hybrid CDL -Human Powered Energy Source Demonstration

Task V Demonstration of a Personal Soldier Fuel Cell Battery Charger

Task VI Vapor Pressure Measurement Facility

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1. "Mobile Battlefield Power Workshop," M.F. Rose, A.K. Hyder, B.D. Guenther, J. Mink, C. Johnson, Directors, ARO Contract #DAALO3-86-D-001, Delivery Order 2263, Nov. 1990.
2. "Joint Directors of Laboratories Pulse Power Audit Team, Final Report," Dr. C.G. Thornton, Chairman, 3 July, 1990.
3. "Mobile Electrical Power Technologies for the Army of the Future--Engines, Power Sources and Electrical Aspects," J. Johnson, ed., National Academy Press, Washington, DC, 1988.
4. "Proceedings of the Prospector Series of Workshops," Prospectors I-XI, Available from the Space Power Institute, Auburn University, AL
5. "Energy Efficient Technologies for the Dismounted Soldier," National Research Council, National Academy Press, Washington, DC, 1997

TECHNICAL TASKS

Task I Thermophotovoltaic Energy Conversion

The objectives of this research are to investigate the key issues governing the use of thermophotovoltaic energy conversion for practical power systems and to establish scaling relations as a function of heat sources.

Thermophotovoltaics is the term applied to the technique for energy conversion whereby the energy emitted by an incandescent source is converted to electrical energy using a photovoltaic cell. There are two distinct approaches to this technique. One uses selective line emitters while the other uses selective filtering, both aimed at taking advantage of bandgap engineered photovoltaic cells. The primary heat source may be from the combustion of fossil fuels, Radioisotope Thermal Generators (RTG) or by concentration of solar energy. The technique is not new. It was proposed by White and Schwartz⁽¹⁾ about 27 years ago and has received periodic attention by several groups^(2, 3, 4, 5) interested in various aspects of the technology. Its potential as a practical power supply is due to the following:

- Certain rare earth oxide emitters are capable of emitting as much as 70% of the total radiated energy in a single line⁽⁵⁾.
- Custom-bandgap tailored photovoltaic cells have demonstrated 30% efficiencies⁽⁶⁾ and are projected to be capable of efficiencies as high as 50%.
- Small scale practical radiating structures have been demonstrated⁽⁴⁾ which are robust enough to withstand shock environments as high as 2000 g's.
- Emitters compatible with the flame temperature of JP-8 appear possible.

The most promising spectral emitters are the rare earth elements in the form of oxides. The 4f electron orbitals, which account for most of the emission and absorption at modest temperatures, lie inside the 5s and 5p electron orbitals. As a result, in crystalline solids, the radiative characteristics of these elements are similar to that obtained for an isolated atom, with narrow band emission, rather than a more broadband continuum superimposed upon a line spectrum. The rare earths most commonly studied are Nd_2O_3 , Ho_2O_3 , Er_2O_3 and Yb_2O_3 . Chubb⁽⁵⁾ has performed a theoretical study of rare earth emitters and concludes that to obtain maximum efficiency, the emission band of the selective emitter must be centered at relatively low energy and suggests that emitters based upon holmium (Ho) and neodymium (Nd) would be good candidates. The optimum temperature of operation would be on the order of 1400K for Nd and some 1500K for Ho. The associated emission would be centered about 0.5 eV for Nd and 0.6 eV for Ho with a bandwidth of some 15% for Nd and 10% for Ho. The radiative process efficiencies were estimated to be 72% for Ho and 55% for Nd.

The low energy for the emission band for Ho and Nd will require the development of new photovoltaic materials specifically tailored with low bandgap energies. The bandgap of the tertiary semiconductor, $\text{Ga}_x\text{In}_{1-x}\text{As}$ can be varied over a wide range by varying the ratio of Ga_x and In_{1-x} in the compound. Similarly, HgCdTe can be fabricated with a wide range of bandgaps.

Silicon ($E_g = 1.29 \text{ eV}$) and Germanium (0.66 eV) are much better matched to emitters of Ytterbia and Erbium. Both of these emitters, however, must operate at higher temperatures, which impose materials constraints and could also contribute to a high thermal signature capable of hostile detection.

An approximation for the radiator size necessary to power a selective array can be calculated from the Stefan Boltzman relationship

$$E = se (T^4 - T_b^4) \text{ W/m}^2 \quad (1)$$

where s is a constant, T is the radiator temperature, T_b is the background temperature, and e is the emissivity of the radiator surface.

For the purpose of estimating radiator sizes, assume $e = 0.75$ and further assume that the background temperature T_b is negligible in comparison to the radiator temperature. For a radiator operating at 1500K , typical of that needed for Ho and Nd, the surface would be capable of radiating 28 W/cm^2 . For Yb and Er (max efficiency at 3000K) the surface could radiate on the order of 450 W/cm^2 . Noting that the sea level solar constant is on the order of 0.1 W/cm^2 , these sources are hundreds of times brighter than the sun. A five kilowatt radiator would be on the order of 178 cm^2 at 1500K and only 11 cm^2 at 3000K . If photovoltaic cells can be made with 25-50% efficiencies, the above radiators could easily provide power on the order of 1-2 kilowatts electric in small compact units. They would require radiator surface areas for thermal management on the order of square meters if the photovoltaic array can be operated at temperatures on the order of 400K . Thermal management based upon conduction and convection will greatly reduce this requirement. Clearly, there would be a tradeoff between output power and the requisite thermal management attendant to any thermal energy converter.

The advantages of "low temperature" emitters is the potential compatibility with a number of fossil fuels, the possibility of using a nuclear heat source, and a lessening of the severe materials constraints associated with operating at temperatures greater than 2500K . The disadvantage, primarily, is the lack of suitable small bandgap photovoltaic cells. There has been little impetus to develop these cells for energy conversion applications due to the spectral content of the solar radiation. The objective of this task is to examine the key elements in a thermal to electric energy conversion approach and establish the scaling laws for those key elements. The key to using this technology in advanced power systems is to produce an effective, efficient, robust radiator first, and,

second, to produce an efficient bandgap matched PV cell. The research on emitter technology encompassed the following:

- Evaluation of emitter samples from commercial sources wherever available to validate theoretical predictions,
- Custom fabrication of emitter structures using fiber/papermaking technology,
- Characterizing of the surface morphology of radiators using both optical microscopy and SEM,
- Evaluation of selected emitter structures for radiation characteristics,
- Evaluation of the effectiveness of each emitter as a function of surface temperature,
- Development of scaling laws and computer models which can be used to estimate the size of radiating units as a function of optical power and temperature,
- Exploration of innovative ways to effectively manage the waste thermal energy and combustion in small units.

The second key element in the efficient use of this technology to produce practical battlefield power units is the availability of photovoltaic materials with energy band gaps matched to the selected emitter wavelength. The Space Power Institute has invested heavily in the facilities necessary to conduct research and development in GaAs technology and is already highly involved in the exploration of InGaAs for a wide range of potential applications. InGaAs is a likely candidate for an efficient band gap matched PV cell. The epitaxial growth of GaAs, InGaAs and InGaAsP on InP or GaAs substrates permits bandgaps varying from 1.35 eV (GaAs) to 0.36 eV (InAs) to be fabricated. However due to funding restrictions, and after consultation with the NASA Lewis Research Center, we decided to enter into a Cooperative Research and Development Agreement (CRDA) with NASA to produce prototype cells for use with our emitters. The Lewis Research Center shares a common interest in this technology for advanced space applications using Radioisotope Thermal Generators (RTG) and solar thermal collectors as heat sources. After a suitable candidate formulation was found for a specific emitter, a custom fabrication facility fabricated the necessary units to test our models and designs. During the course of this work, Dr. Chubb, the NASA principal scientist interested in thermophotovoltaics was in residence at the Space Power Institute as a Distinguished Visiting Research Scientist.

As part of this task, we sought to accomplish the following specific items related to optical-to-electrical energy conversion:

- Investigate, experimentally and theoretically, bandgap tailoring in the InGaAsP system over the range of parameters of interest and over a range compatible with battlefield fuel combustion temperatures,
- Conduct theoretical studies of thermal transport in the InGaAsP system to clarify any issues which may impact the thermal management of PV arrays and to fabricate experimental samples sufficient to evaluate predictions.

Accomplishments

The following were accomplished during the duration of this research program within task I:

- Compiled enormous database for thermophotovoltaic energy conversion technology, including compact burner technology, combustion in small systems, and fuels,
- Developed thermophotovoltaic laboratory complete with unique diagnostics capability, including spectroscopy from the UV to the far IR,
- Investigated several structures for producing selective emitters and selected composites made using paper making technology for development; established the technology to produce both blackbody and selective emitter structures of arbitrary size and shape using fibrous rare earth oxides and silicon carbide in composite form,
- Built small combustion test stand with calibrated flow meters to measure combustion parameters, etc.,
- Characterized line emission from the oxide samples which can be used in the photoconversion process as a function of temperature and percent structural material: characterized radiant output power density of composite emitters as a function of distance from source to target and as a function of wavelength,
- Established CRDA relationship with the NASA Lewis Research Center and from CRDA relationship, received 3 InGaAs photovoltaic cells with differing bandgaps; characterized cells under selective line emission,
- Verified reduction in fuel requirements using selective line emitters both theoretically and experimentally; Achieved 20% radiant to electrical power conversion efficiency using erbia composite emitter in conjunction with 1st generation 0.75 eV bandgap InGaAs PV cell,
- Performed evaluation of various "mantle" geometries and established the feasibility of obtaining stable combustion in the proposed hybrid burner configuration; Integrated a selective emitter structure into the burner testbed,
- Developed a parametric model for evaluating TPV system thermal management issues; Developed a turbulent diffusion model for hybrid configuration; The work is complete, has been used to model several system configurations and a PhD thesis has been written which thoroughly documents the results,

- Established the technology to produce emitter structures with "finned or star" shape for optimum coupling to the combustion flame; Characterized line emission from the oxide samples out to 10 microns using the new spectrometer laboratory purchased using DoE funds; Established structural materials of choice (Al_2O_3) which represents a good trade between strength and spectral purity; Built and characterized mixed metal oxides emitters that are stronger and can be tailored to match a wide range of photovoltaic converters, essentially matching the emission to the quantum response of the cells,
- From CRDA relationship, second generation cells using InGaAs were characterized and 100 cm^2 purchased from the Research Triangle Institute,
- Built and conducted preliminary testing of a vapor pressure facility for determining the lifetime of selective emitters. Testing to 1100 K resulted in failure of heat shields. Problem will be addressed and fixed in the coming year,
- Built a "benchtop" TPV system to characterize losses and clarify system issues. Model clearly shows that the major issue is the thermal recuperation of energy left in the combustion gasses after passing through the mantle structure. Completed an experimental PhD thesis on "benchtop" model, thoroughly documenting the results.
- Provided numerous samples to other ARO contractors.

The details of these accomplishments are described in the technical papers, theses and dissertations listed below which were generated in this task.

Technical Papers/Conference Proceedings

"High Temperature Emitters for Thermophotovoltaic Power Systems, P. L. Adair and M. F. Rose, " Proceedings of the 36th Power Sources Conference, New Jersey, 1994

"Composite Emitters for TPV Systems," P. L. Adair and M. F. Rose, AIP conference Proceedings No. 321- The First NREL Conference on Thermophotovoltaic Generation of Electricity, American Institute of Physics Press, 1994

"High Temperature Emitters for Thermophotovoltaic Power Systems for Aerospace Applications," M. F. Rose, and P. L. Adair, 33rd Aerospace Sciences Meeting and Exhibit

"An Experimental Investigation of Hybrid Kerosene Burner Configurations for TPV Applications," K. L. Schroder, M. F. Rose, and J. E. Burkhalter, AIP conference Proceedings No. 321- The First NREL Conference on Thermophotovoltaic Generation of Electricity, American Institute of Physics Press, 1994

"Selective Emitters for Thermophotovoltaic Power Systems for use in Aerospace Applications," M. F. Rose, P. Adair, Ken Schroeder, AIAA Journal of Propulsion and Power, Vol. 12, No. 1, 83-88, 1996

"Competing Technologies for Thermophotovoltaics," M. Frank Rose, Proc. 2nd NREL Thermophotovoltaic Generation of Electricity Conference, Colorado Springs, Co. July 1995

"Increased Thermophotovoltaic Systems Efficiency Using Selective Emitters," P. Adair, M. F. Rose, Proc. 30th IECEC Vol. 1, pp. 503-508, 1995

"A Parametric Study of TPV Systems and the Importance of Thermal Management in System Design and Optimization," K. Schroeder, M. F. Rose, and J. E. Burkhalter, Proc. 30th IECEC, Vol. 1, pp. 719-724, 1995

"Increased Thermophotovoltaic System Efficiency Using Selective Line Emission," P. Adair and M. F. Rose, 30th Intersociety Energy Conversion Engineering Conference 1995

"Extended Use of Photovoltaic Solar Panels," G. E. Gauzzoni and M. Frank Rose Proc. of the Second NREL Conference on Thermophotovoltaics, Colorado Springs 1995

"Novel Thermophotovoltaic Composite Selective Emitter Design," P. Adair, Z. Chen, and M. F. Rose, 37th Power Sources Conference Symposium, 1996

"Photoelectric Conversion Efficiency for InGaAs Photovoltaic Cells illuminated by Composite Selected Emitters," P. Adair, Z. Chen, and M. F. Rose, 31st IECEC Conference, August 1996

"Selective Emitters for Thermophotovoltaic Energy Converters-A Study based on Materials Prospects," Z. Chen, P. L. Adair, and M. F. Rose, 37th IECEC Conference, August 1996

"Fabrication of Fibrous Er_2O_3 Composites for Heat to Light Conversion," Zheng Chen, P. L. Adair, and M. F. Rose, High Temperature Materials Science, Vol. 37, P 71-79, 1997

"Multiple-Dopant Selective Emitters," Z. Chen, P. L. Adair, and M. F. Rose, Proc. Third NREL Conference on Thermophotovoltaic Generation of Electricity, AIP Conference Proceedings 401, Colorado Springs, CO 1997

"TPV Power Generation Prototype Using Composite Selective Emitters," P. L. Adair, Z. Chen, and M. F. Rose, Proc. Third NREL Conference on Thermophotovoltaic Generation of Electricity, AIP Conference Proceedings 401, Colorado Springs, CO 1997

"Effect of Temperature Gradient on Thick Film Selective Emitters," D. L. Chubb, B. S. Good, E. B. Clark, and Z. Chen, Proc. Third NREL Conference on Thermophotovoltaic Generation of Electricity, AIP Conference Proceedings 401, Colorado Springs, CO 1997

"An Improved Model for TPV Performance Predictions and Optimization," K. L. Schroeder, M. F. Rose, and J. E. Burkhalter, Proc. Third NREL Conference on Thermophotovoltaic Generation of Electricity, AIP Conference Proceedings 401, Colorado Springs, CO 1997

"Investigation of Energy Conversion in TPV Power Generation Prototype using Blackbody/Selective Emitters," Z. Chen, P. L. Adair, and M. F. Rose, Proceedings of the IECEC, AIChE, Page 1097-1106, Honolulu, Hawaii, July 27-August 1, 1997

"Fibrous Materials for Selective Line Emission Application in a Thermal-Electrical Energy Conversion System," Z. Chen, P. L. Adair, and M. F. Rose, Proceedings of the Space Technology and Applications International Forum, AIP Conference Proceedings 387, Albuquerque, NM, 1997

Theses and Dissertations

"Experimental Investigation of Composite Emitters used in Thermophotovoltaic Power Generation," Thesis submitted to the Graduate School in partial fulfillment of the requirements for the degree **Master of Science** by P. L. Adair

"Design and Fabrication of a Thermophotovoltaic Power Generation Unit," P. L. Adair, Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of **Doctor of Philosophy** in Electrical Engineering, June 1997

"Performance Optimization of Thermophotovoltaic Systems," K. L. Schroeder, Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of **Doctor of Philosophy** in Aerospace Engineering, June 12, 1998

Personnel

The following is a listing of the staff and students who were employed totally or in part on this task:

M. Frank Rose, PI and Director Space Power Institute
Dr. Peter Adair, (Graduated PhD June 1997)
Kenneth Schroder, (Graduated PhD June 1998)
Dr. Z. Chen, Post Doctoral Fellow
Mark Dickman, Graduate Research Assistant
Swati Sharma, Undergraduate Assistant
Jessica Rawls, Undergraduate Assistant

Technology Transfer to the Industrial Sector

The research effort was successful in producing large area, highly efficient optical emitters and bandgap matched PV cells. As a result, we provided samples and emitter fabrication know-how to JX Crystals, Quantum Group, Essential Research, and Babcock and Wilcox Inc. There is now a continuing effort with Babcock and Wilcox for advanced development of the emitters invented in this program.

Patents

From this work, three Patents have been issued relating to emitter technology for use in Thermophotovoltaics. Negotiations are currently under way with Babcock and Wilcox, Inc. for a license. The patents are:

"Composite Narrow Band IR Emitters," 1995, 5,447,786

"Preparation of Selective Line Emitters," 1997 5,630,974

"Selective Infrared Line Emitters," 1998 5,780,370

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7. L.D. Woolf, "Solar Photothermophotovoltaic Energy Conversion," Proc. 22nd Intersociety Energy Conversion Engineering Conference, ISBN 0-930403-29-0, 1987, pp. 88-93.

Task II Composite Fiber Electrode Structures for Chemical Energy Storage and Production

The objective of this task is to research, exploit and refine novel material fabrication techniques for the microstructural design of electrodes for use in fuel cells, batteries and liquid double layer capacitors, and to establish predictive performance envelopes for each of these devices based on experimentally verified kinetic, catalytic, transport and microstructural attributes of the electrode.

From the cadre of available and envisioned mobile power technologies, electrochemical systems are ubiquitous and often preferred due to their simple and efficient modes of operation. Moreover, electrochemical systems are relatively well understood, compact, robust and unobtrusive in nature. While the theoretical energy density for almost any electrochemical device can be readily calculated from e.g., the mass of reactants; the energy and power densities attained in practice are generally much lower and attributed to inefficiencies arising from microscopic physical processes occurring at, or within, the electrode.

The research conducted in this task explores the fabrication and microscopic physical attributes of a new composite fiber electrode (1,2,3) concept designed to enhance the performance of various devices including: liquid electrolyte fuel cells; solid polymer electrolyte fuel cells; Li/SOCl₂ batteries; and liquid double layer capacitors.

Because of the central role provided by the electrode in many different types of electrochemical devices, this research has lead to the development of new microstructurally engineered electrodes offering substantial performance improvements. The results of this research task, therefore, transcend that of a single device or design to impact upon an entire range of electrochemical devices.

The Composite Electrode Concept

In general, it is difficult to find materials with both high surface area and high electrical conductivity. For the applications explored in this research, high specific surface area and high electrical conductivity are desired characteristics. This situation arises because high surface area materials such as activated carbon powders are only moderately conductive and have a low density while the higher conductivity materials such as metals are less porous and have higher density giving them much lower specific surface areas (i.e., m²/g). For these reasons, a composite electrode was envisioned and pursued to combine the high specific surface areas of activated carbons along with the higher electrical conductivities of metals.

Because activated carbons and metals do not form strongly adhesive bonding arrangements to one another, have different thermal expansivities, and possess different densities and tensile properties, they do not mix well when dry or provide good adherence

to metal substrates under normal conditions. Moreover, mixtures of activated carbon powders and metal powders do not provide sufficient interparticle contacts to significantly reduce electrode resistivity unless high levels of metal are used in conjunction with significant levels of compressive pressure on the resultant powder bed. To address this problem a unique method of creating composite electrode structures was invented. Using this procedure, high surface area activated carbon fibers (ca. 2 mm in diameter) are placed in an agitated liquid dispersion using an appropriate surfactant and solvent. To this mixture metal fibers such as nickel or stainless steel fibers (2 mm in diameter) and cellulose fibers of similar size are also added. The homogeneous mixture is then filtered and dried to form a randomly oriented and free-standing sheet of "metal-carbon composite paper."

These papers are then affixed to metal backings using a high temperature annealing procedure which removes the cellulose while sinter-bonding the metal fibers to one another and to the metallic backing/collector. The preparation and treatment conditions required to carry out this procedure are particularly novel, have been extensively optimized (1), and presently form the basis for four patents. With only a subtle variation in processing conditions, the porosity and void volume of the finished electrode can be varied by adjusting the amount of cellulose in the precursor paper (which is removed on sintering) and/or the level of mechanical pressure used during sintering. This particular attribute of the electrode synthesis procedure is highly desirable and allows the void volume to be selected over a wide range so as to enhance the heat and mass transfer rates in the electrolyte (viz., important for fuel cells and capacitors) or the accommodation of precipitates (viz., important for high power density lithium batteries, among others).

Since particles of carbon powder must contact one another to form an electrically conductive network, it is clear that the high aspect ratio possessed by fibrous electrodes provide the key structural ingredient necessary for the fabrication of both high porosity and high connectivity/high conductivity electrode structures. This attribute is not available from powdered precursors. Furthermore, the interfiber/intermaterial contacting is quite extensive and does not require external mechanical pressure after preparation to maintain this contact as would be required for a bed of powdered electrode material. This important attribute of the Auburn composite fiber electrode allows scaling to larger cross-sectional areas and lower sheet resistances in the absence of heavy-walled packaging materials that would otherwise be required for similar bed geometries of powdered electrode materials.

Electrochemical testing of the composite electrode in the form of cyclic voltammetry, AC impedance and potential step analyses of single capacitor electrodes reveals that the optimized structure provides good accessibility to the electrolyte, good contacting to virtually all the carbon retained within the electrode, and relatively little mechanical pressure dependence on electrode performance. Energy densities approaching 240 kJ/(kg of electrode only) have been obtained using high breakdown voltage organic electrolytes (ca. 19.0 F/g of carbon at 3.5-5.0 volts) with characteristic discharge times of ca. 1-3 seconds across a dead short. More conductive electrolytes such as H_2SO_4 , KOH or

Na₂SO₄ provide capacitances of 50-80 F/g of carbon at breakdown potentials from 1.2 to 2 volts resulting in energy densities from 50-160 kJ/(kg of electrode only) at discharge times from 0.5 to 0.005 seconds.

In summary, the Auburn composite electrode structure is a promising substrate for capacitors, fuel cells and high power density batteries. These electrodes possess high specific surface area in finished form, are readily accessible to gases and electrolytes, can be prepared with variable void volumes, are amenable to flow-through designs to enhance heat and mass transport, can be prepared in almost any conceivable size and shape, have electronic properties which are not strongly dependent on mechanical pressure and will accommodate various levels of solid precipitates without significant loss in surface area. The unique attributes of these electrodes stem from the high aspect ratio of the fibrous precursors which allows the entrapment of one fiber within the sinter-bonded network of the other. The resulting composite has good connectivity between the different material constituents and possesses "averaged physical properties" which were once thought to be mutually exclusive. This task researched the application of this unique technology to batteries, fuel cells, and electrochemical capacitors of use within the Army's power sources.

Accomplishments

- Common issues for energy storage and production have been identified as microfiber corrosion, heat/mass transport, tailoring of composite microstructure, microfiber contacts to secondary material and flow-through monolithic electrode structures.
- For alkaline fuel cells, several experimental electrodes have been made using 850 m²/gm activated carbon and 2 micron nickel. Tafel kinetics, polarization, and mass transport studies are beginning for these samples.
- For chemical double layer capacitors, several electrodes have been fabricated which show an increase of 20-30% increase in capacitance over previous electrodes. The best values are on the order of 70 farads/gram of carbon.
- Numerous electrode formats, which enhance heat transfer, in monolithic fuel cell/battery applications have been investigated with success. Catalyst supports have also been incorporated in some structures.
- Several new electrode structures have been conceptualized for use in Ni/Cd, Ni/H₂ and Ni/hydride battery systems which may impact current Army inventory.
- Successfully demonstrated new types of fuel cell electrodes based upon an "extended three-dimensional reaction zone" achieved using intermingled phases of electrocatalyst along with thin-layers of electrocoated Nafion
- Developed an electrophoretic coating procedure for conformally coating platinum-impregnated metal fiber-carbon fiber composites with thin-layers of Nafion-117

- Characterized performance of new electrodes
- Developed equivalent circuit models to explain the observed impedance characteristics associated with composite electrodes.
- Developed peroxide decomposition electrodes based on composite microfibrous materials.
- Developed microfibrous electrode structures to be used as the anode in lithium batteries.
- Thoroughly characterized the electrodes using half cell cycle tests vs a lithium electrode.
- Provided samples to Dr. Terrill Atwatter at CECOM for evaluation.
- Provided samples to Dr. Kim Kinoshita at the Lawrence Berkeley Laboratory for evaluation.
- Test results from both laboratories promising.

PEM Fuel Cells

PEM membrane-electrode assemblies (MEA's) are being developed whose electrodes are platinum-catalyzed, activated carbon/nickel composite fiber electrodes; the membrane is Nafion. Preliminary optimization of the electrode structure and MEA assembly process has resulted in current densities of nearly 180 mA/cm² at a cell voltage of 0.6 V and a temperature of 55 C. Reference electrode studies have shown that the predominant voltage loss is at the cathode. The three dimensional nature of the composite electrodes, enhanced by nickel fiber overlayers provides a built-in plenum for gas flow lateral to the electrode surface, which is required for the system design.

Lithium-Ion Batteries

Recent literature has shown excellent activity of pitch-based carbon fibers for lithium intercalation in lithium-ion batteries. A series of composite electrodes has been made from pitch-based carbon and nickel fibers to optimize structure for specific energy and to perform half-cell characterizations. A glove box facility was set up, and a preliminary half cell experiment was conducted. Initial results show activity for lithium intercalation. Sintering studies showed good compatibility of these composite electrodes with both expanded nickel and copper current collector screens.

Ultracapacitors

ARL has shown excellent power densities are achievable from hydrated ruthenium oxide electrochemical capacitors. ARL shipped a sample of this material to AU for fabrication into microfiber electrodes and preliminary characterization. Capacitance values of 423, 344, and 268 farads per gram of active material were measured after the electrode had been in potassium hydroxide for 1, 2, and 15 days. Impedance measurements showed that the loss of capacitance was due to structural changes rather than loss of the active material. Further efforts are underway to optimize paste-casting efforts and structures for uniformity in basis weight. These efforts will be transferred to acid-resistant metal microfiber systems and stable higher capacitance acidic electrolytes.

Oxygen Electrodes for Zinc-Oxygen Batteries (Opportunity for Soldier Systems)

Zinc-oxygen primary batteries have demonstrated high (> 400 Wh/kg) specific energies in recent testing at ARL, and therefore may be of use for 100-150 W soldier systems and for covert power missions. The composite fiber technology has the potential for reducing the oxygen electrode thickness from about 20 mils to less than 5, without a performance penalty. Non-ARO supported work has therefore been undertaken to apply the oxygen diffusion electrode for various applications from hydrogen peroxide to zinc-air batteries. The difference between peroxide and oxygen electrodes is that the latter must have a peroxide decomposition catalyst for efficient operation. A process was adapted from the literature which deposits an active manganese hydroxide catalyst on the carbon fibers via an incipient wetness-hydroxide precipitation method. Initial measurement of peroxide decomposition activity was very encouraging. This effort has direct application to the soldier system as a reliable and robust primary battery system.

Personnel

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Technical Publications

"Air Electrode: Identification of Intraelectrode Rate Phenomena via AC Impedance," J. Electrochem. Soc. 142(12), 1995

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"Electrodeposition of Nafion onto Electrode Structures," B. J. Tatarchuk, G. Swain, X. Xu, J. Wang, and R. Killough, Presented/Published at the Prospector VII, an ARO and Auburn University/Space Power Institute Sponsored Workshop on "Small Portable Fuel Cells, Durham, North Carolina, October 31-November 3, 1994

"Electrochemical Reduction of Oxygen at "Electrocoated" Nafion-Modified Metal-Carbon Composite and Platinum Electrodes," G. M. Swain and B. J. Tatarchuk, J. Electrochem. Soc. 140 (4), 1026, 1993

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"Impedance Modeling of Metal Fiber-Carbon Fiber Composite Electrodes for Electrochemical Liquid Double Layer Capacitors," D. R. Cahela and B. J. Tatarchuk, Proceedings of the 37th Power Sources Conference, Cherry Hill, NJ, June 17-20, 1996

"Oxygen Electrodes Based on Composite Microfibrous Materials," R. F. Smith, S. Ahn, and R. A. Putt, Proceedings of the 37th Power Sources Conference, Cherry Hill, NJ, June 17-20, 1996

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"Overview of Electrochemical Capacitors," D. R. Cahela and B. J. Tatarchuk, IECON'97, New Orleans, Louisiana, November 9-14, 1997

"Impedance Modeling of Nickel Fiber/Activated Carbon Composite Electrodes for Electrochemical Capacitors," D. R. Cahela and B. J. Tatarchuk, IECON'97, New Orleans, Louisiana, November 9-14, 1997

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1. Tatarchuk, B.J., et al., US Patent Application, May, 1989, #07/356,861, and other subsequent/associated US and Foreign filings.
2. Kohler, D. A., Zabasajja, J., Rose, M.F., and Tatarchuk, B.J., J. Electrochem. Soc., 137(6), 1750-57, 1990.

Task III. Electrical Characterization of Exploding Liquid Metal Jets

The objectives of this task are to investigate the electrical behavior of exploding liquid metal jets and to determine their potential as a repetitive opening switch for high pulsed power applications.

High power switching is the key element in controlling the storage and distribution of electrical energy in high power systems. Recently, pulsed power systems in the 100 TW class have been built for applications such as weapons effects simulation and inertial confinement fusion. That power level represents roughly 100 times the total output of the US power grid. In general, machines of this class may utilize both capacitive and inductive storage depending upon the specific technique employed. Inductive storage units are on the order of 10 times more energy dense than comparable capacitive storage units. While capacitive stores require closing switches to release the stored energy, inductive storage units must employ an opening switch to interrupt current flow and transfer the energy to the desired load circuit. Opening switch technology for ultra high power applications is confined to a few techniques and nearly impossible for modest repetition rates. As a result, the lack of an acceptable opening switch, particularly repetitive ones, has long inhibited the beneficial use of inductive stores for routine applications. Since inductive stores are considerably more compact than similar capacitive units, the availability of a simple reliable repetitive opening switch is of paramount importance to the high pulse power community and would allow the development of far smaller, more compact machines for a variety of weapons applications of interest to the Army.

There are many techniques for opening switches, most of which are described in a book edited by Guenther, Kristiansen and Martin.⁽¹⁾ This book constitutes an excellent tutorial as well as an in-depth literature review of the subject of opening switches and their applications. In general, the repetitive switches are "low power devices" or "moderate" power devices such as Thyratrons and Crossatrons (see Chapter 3, reference 1) which are current limited but can open against modest driving point voltages. These switches are of limited use since inductive storage units for high-energy applications are inherently high current, high inductance devices. At the other end of the scale, specialty opening switches employing plasma dynamic effects (Chapter 5, 6, 7, reference 1) are capable of interrupting kiloamperes to megaamperes at megavolt potentials. Unfortunately, these techniques are not amenable to rep rate applications.

There is one class of opening switch, exploding electrical conductors, (Chapter 8, reference 1) which is used routinely to interrupt currents in the multi-megaampere range on time scales from nanoseconds to microseconds. The principle of operation is simple. An electrical conductor, consisting of metallic foil or wires, experiences a rapid rise in resistance as a result of ohmic heating. The heating is a result of the current that the element is intended to interrupt. As the process proceeds, the element passes through melting and subsequent vaporization in extremely rapid succession (depending on nature of store). As a result, the electrical resistance of the "conductor" package changes by

several orders of magnitude in a time governed by the circuit and the "conductor" parameters.

Reinovsky (chapter 8, reference 1) describes in detail the theory and application of fuse technology in high pulsed power machines. Since the process is explosive, the repetition rate is at best one every few minutes. A conversation with Professor G.A. Mesyats of the Institute of Electrophysics, USSR Academy of Sciences, revealed the use of an opening switch based upon exploding wires in a commercially available x-ray machine named VIR-1.5M. The switch must open at 100 kv - 20 kA. The pulse repetition rate is once every 8 seconds and the exploding wires have an automatic feed system. He has made the switch and reloading mechanism reliable enough for commercial applications and it operates in the 2×10^9 watt range.

The above reference and sources such as the proceedings of the pulse power conferences clearly shows that "exploding" conductor technology is capable of reliable, repeatable operation in single shot high power machines. Their utility is limited by the necessity for replacement of the conductor package after each switch event. It seems obvious that since the switch conductor must pass through a liquid phase, it would be more energy efficient for the conductor to begin as a liquid. An ideal candidate for such an application is the liquid metal, mercury. Among the more obvious potential advantages are:

- Less energy lost in the switch since the solid-liquid transition is absent,
- Liquid metal jets are inherently self-replacing since they are extruded from an orifice under pressure,
- High velocity jets can cross substantial gaps in short times offering the potential for modest repetition rate, orientation independent, opening switch applications,
- Numerous jets can be used simultaneously allowing real-time variations in the total switch conductivity,
- Selected jets can be turned on and off thereby varying the current-time capability of the total package, i.e., many jets might be used in the charging phase of the inductive store and several turned off to start the switch process by shutting off the flow to those orifices, and
- The jets always have uniform material parameters due to homogeneity of the liquid metal.

In view of the potential for application of exploding liquid metal jets as a repetitive opening switch, this research task investigated the electrical characteristics of liquid mercury jets as they are driven through the liquid-vapor transition due to ohmic heating.

Accomplishments

In Task III, the following has been accomplished:

- Established database on the properties of Mercury and other liquid metals during high-rate ohmic heating,
- Investigated Action Integral for liquid metal jets including non linearities,
- Developed a jet test facility which allows variation of pressure and jet length, and provides an enclosure to contain by-products from the jet explosion,
- Developed a reliable diagnostic system, immune from the noise which is always present in rapidly changing inductive systems, using exploding copper wires in place of liquid metal jets,
- Established jet velocities as high as 7.5 m/s, which would allow rep-rate switching of several hertz in an opening switch mode,
- Made temporally and spatially resolved measurements of plasma temperature in the exploding jet,
- Increased peak current in the exploding jet to study switching capability at currents up to 125 kA,
- Employed multiple jets (up to 4) in horizontal and vertical positions and compared switching performance to that of single jets,
- Examined the effect of different ambient gas species on switch performance.

In 1996, this task was terminated due to lack of interest within the Army community in electric gun technology. The following publications contain details of the above accomplishments.

Publications

"Switching and Scaling Behavior of an Exploding Mercury Jet," R. Criss and M. F. Rose, Proc. 10th IEEE Pulsed Power Conference, July 1995

"Spatial & Temporal Development of Emissions from an Exploding Mercury Jet," R. Criss, M. F. Rose, IEEE Trans. on Plasma Science, 1995

"Evaluation of Liquid-Metal Jets as the Conductor in a Rep-Rated, Exploding-Fuse Opening Switch," W. E. Ansley and M. Frank Rose, IEEE Trans. on Magnetics, May 1996

Theses and Dissertations

"Evaluation of Liquid Metal Jets as the Conductor in a Rep-rated, Exploding-Fuse Opening Switch", thesis submitted to The Graduate School in partial fulfillment of the requirements for the degree of Master of Science by W. E. Ansley

Personnel

Dr. Randy Criss (Post Doctoral Fellow)
Dr. Steven Merryman (Post Doctoral Fellow)
Mr. William Ansley (Master of Science Candidate)

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Task IV Pulsed Power Demonstration

Introduction

For pulsed applications, chemical double layer capacitor sources can be used to provide high power pulses (100's of watts) for short periods of time (seconds to minutes) while being charged from low power sources (a few watts) such as batteries, hand-cranked generators, or possibly solar arrays. However, the voltage decay as the capacitor source discharges is undesirable for many applications. Thus, the purpose of this research effort was to develop and demonstrate power systems with a capacitive power source such that a constant output voltage/power level is maintained while the capacitor source voltage decays. It is desired to control the voltage from the initial charge voltage, V_0 , down to $V_0/2$. A controllable voltage range of this order would permit 75% of the initial stored energy to be drawn from the capacitor source while providing a constant output voltage/power pulse. Using commercially available DC-DC Power Converters, we evaluated supercapacitor power sources for Army applications where the dc-dc converter was used to maintain a constant output voltage level even though the voltage on the capacitor decayed as energy was drawn from the device. For system demonstration purposes, a capacitor was charged at a low power rate from a hand-cranked generator and

discharged at a higher power rate through a dc-dc converter that maintained a constant output voltage level.

System Description

In this research effort, a portable power source system was built and tested as shown in Figure 1. In this configuration, the capacitor power source was charged from a handcranked generator and discharged through a dc-dc converter to a load of approximately 100 W. The low power source used to charge the capacitor bank could also have been a battery, solar cell, or some other source with a limited discharge rate. For demonstration purposes, the loads used in these tests consisted of a television set, a light bulb, and resistive loads to simulate realistic conditions. Actual loads for military applications would likely be field radios or other devices for communications and video transmission systems.

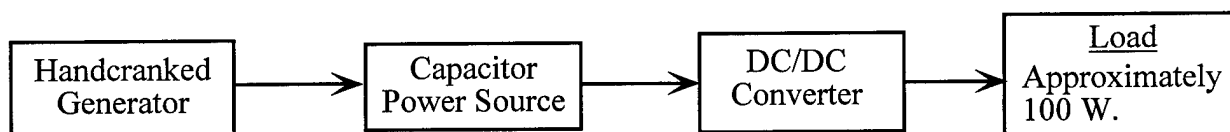


Figure 1. Typical System Schematic.

The dc-dc converters used in these tests were commercially available modules manufactured by VICOR which had the characteristics shown in Table 1.

Table 1. DC-DC Converter Characteristics

Parameter	Module #1	Module #2
Input Voltage	24 V nominal	12 V nominal
Control Range	21-32 V	10-20 V
Output Voltage	28 V	12 V
Input Power	135 W	100 W
Output Power	100 W	75 W

Results

Tests to determine the operating range of the dc-dc converters were performed by discharging a capacitor bank into resistive loads. Figure 2 shows the voltage waveforms for the dc-dc converter with the 28-V output. The capacitor voltage is the input to the converter and it can be seen that the output voltage was maintained at a constant level of 28-V until the capacitor voltage dropped to approximately 18 V.

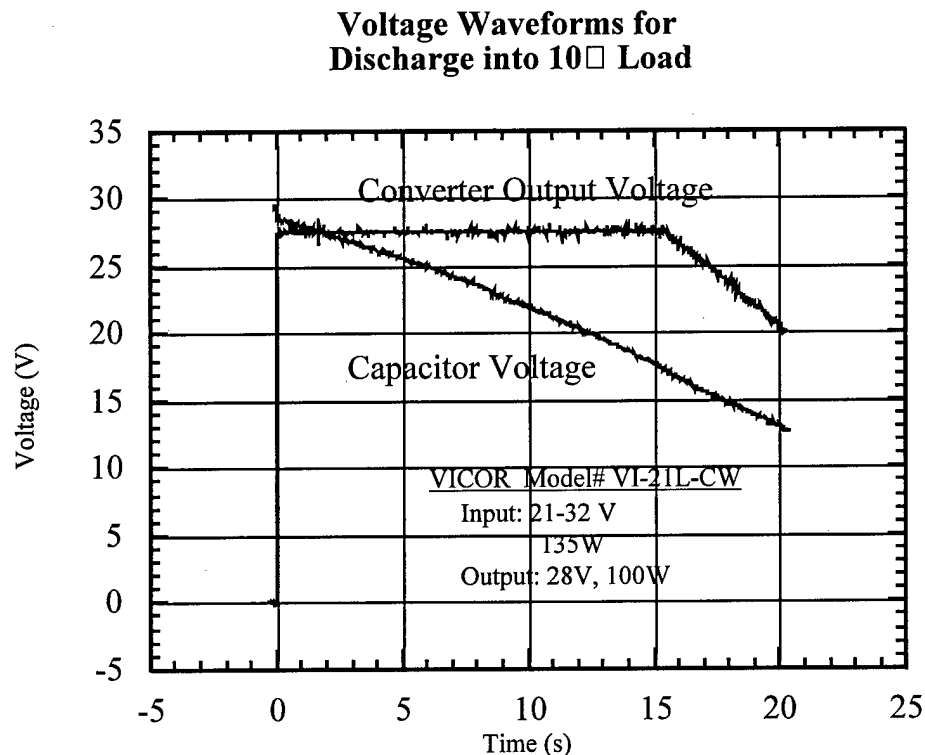


Figure 2. Voltage Waveforms for DC-DC Converter

The portable power system (dc-dc converter, approx. 8-F capacitor, and handcranked generator) used in these tests is shown in Figure 3.

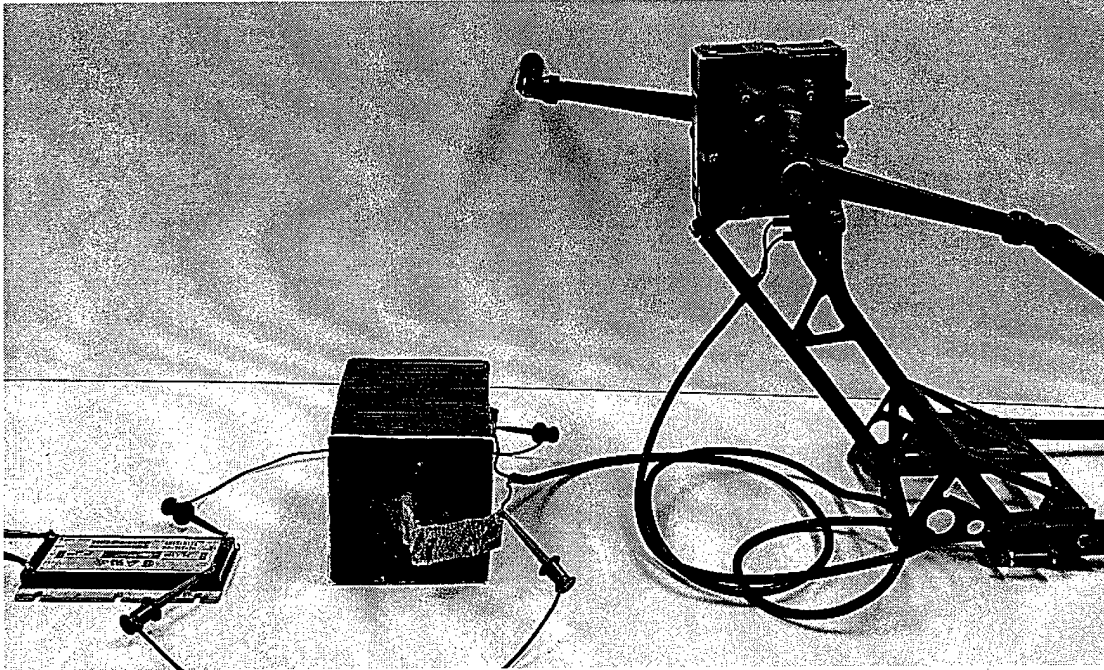


Figure 3. Portable power system

Using the handcranked generator with an output power of approximately 20 W, it took about 165 s to charge the capacitor to its rated voltage of 28 V. For tests using these converters, it was possible to discharge the capacitors at 75-W or 100-W power levels which was 4-5 times greater than the power level used to charge the devices. These systems demonstrated the capability to supply high power loads at a constant voltage or power level from a capacitor source that was charged at a low rate.

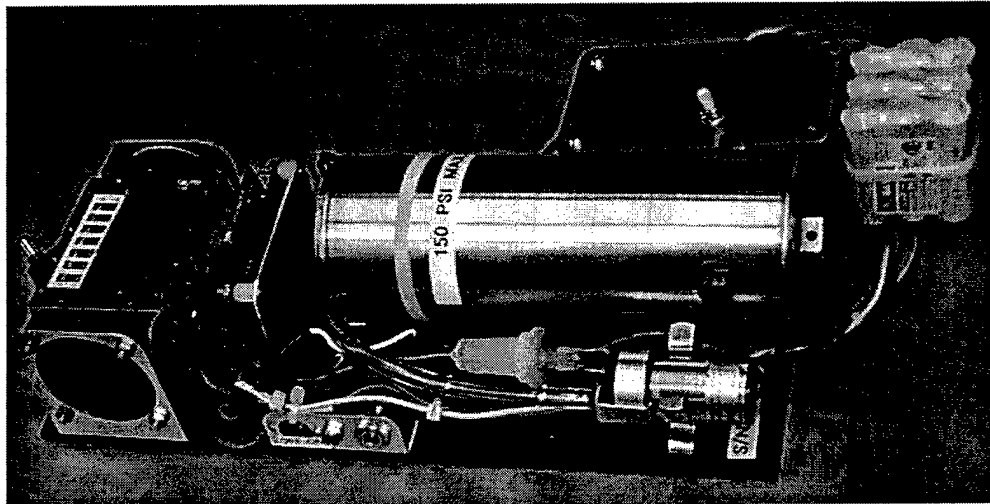
Conclusions

Capacitor power sources can be used to provide high power pulses for low duty cycle Army applications. Using the appropriate dc-dc converter technology, they can be used to deliver high power levels for tens or hundreds of seconds at a constant output voltage and/or power level. The capacitor devices can be charged at a low power source such as a handcranked generator or battery and discharged at much higher power levels. A system of this type would be suitable for many Army applications such as the power source for portable field radios, video transmission systems, or other communications equipment which benefit from operation at higher power levels. For many of these systems, the higher power level at which the system operates results in increased capability, as more information is capable of being transmitted in high power pulses. The major accomplishments are:

- Assembled components from ARL and capacitor built in house.
- Hand cranked generator used to charge chemical double layer capacitor producing greater than 100 W for minutes.

Task V Soldier Portable Personal Battery Charger

This task was added in consultation with the ARO Program Director in the fall of 1997. There is an enormous amount of interest in simplifying the logistics tail associated with batteries as a source of energy for the military. Breakthroughs in electronic technologies/sensor technologies are moving rapidly to expand the capability into previously forbidden regimes. As a result, sophisticated systems are proliferating rapidly in the battlefield giving the Individual Dismounted Soldier enormous capability. The requisite battlefield power technology determines how long these sophisticated systems will be able to perform in the field and how much of the mass that a soldier must carry must be devoted to power. For some missions, the soldier must decide whether to take more batteries to insure operability of systems or to take more ammunition or food to maintain his fighting capability. Advances in power technology are slower than advances in electronic suite capability due to safety issues, environmental concerns, and the limits on the specific energy and power of energy sources. Requisite power technology is based on 30+ year old technology (i.e., batteries and motor-generators) which has definite limits on specific power and energy. There are two approaches to improving the soldiers energy supply. Power/energy requirements may be reduced by optimum power/energy utilization or by the introduction of more energetic sources. Several new technologies are emerging which promise significant improvement over existing technologies. Without improvements in power/energy devices, missions employing sophisticated technology will be limited due to power and will require commanders to make decisions trading mass of power/energy system against mass of ammunition and food for long missions. Fuel cells have been demonstrated with efficiencies higher than 50%. A combination fuel cell and rechargeable battery, if feasible from a specific power and energy point of view, would allow the soldier greater autonomy in the battlefield while reducing the logistics associated with rechargeable batteries. The purpose of this task was to design, build, and test a hydrogen PEM fuel cell suitable for use as a personal charger.



Cell Stack

Hydrogen Store

Figure 4 Photograph of fuel cell stack, hydrogen storage and charging and battery supply used to Demonstrate Soldier Portable Power

Progress to date

The goals of the program were to design and build a device that was within the form and function designated as representative of advanced power concepts of use to the dismounted soldier. The following were accomplished:

Designed and contracted with H-Power Inc. to build a nominal 10W fuel cell,

Designed and tested circuitry to serve as a battery charger

Operated the fuel cell as a charger and demonstrated its utility to several Army groups.

Task VI Development of a vapor pressure measurement facility

Introduction

Evaporation rates and vapor pressures are critical data for determining the lifetime of materials in vacuum environments such as outer space. Examples include thin film oxides which are used as protective coatings of optical components and photovoltaic materials. There is only limited vapor pressure data available on low vapor pressure, high temperature materials. Therefore, both the experimental method to measure vapor pressure of these materials and the facility established as a result of this contract are intended to serve as valuable tools for obtaining these data.

There are several methods of measuring the vapor pressure of substances in the literature and Langmuir's method of evaporation from a free surface is one of these methods which was adapted in this work. It consists of measuring the mass loss rate of an evaporating sample in vacuum. In this method there are several assumptions that must be satisfied. One of these assumptions is that the background density in the vacuum chamber is much smaller than the density due to the evaporating sample. This can be easily achieved if the pumping rate is much higher than the evaporation rate of the sample. If the vacuum system is capable of sustaining ultra high vacuum i.e., pressures of 10^{-8} to 10^{-10} torr in the chamber, then the above assumption is satisfied. We have used a vacuum chamber pumped by a cryogenic pump and obtained pressures of 10^{-10} torr in the chamber. The second assumption is that the molecules leaving the sample's surface will behave like free molecular flow, and they do not collide. This is satisfied by placing the detector close enough to the sample that the distance between the sample and the detector is much smaller than the mean free path of the molecules.

The most important assumption in this work is that the temperature across the sample is uniform. Therefore, this work mainly includes design and construction of an automated temperature control system, where the sample temperature is monitored constantly at different locations, and a feedback system controls the current (power supply output) supplied to the tungsten filaments used to heat the sample. Hence, with uniform sample temperature, a uniform evaporation rate across the sample results. If the temperature is constant, and the free molecular flow assumption applies, the evaporation rate will be constant. Therefore by monitoring the evaporation rate as a function of time at different temperature levels yields evaporation rate data as a function of temperature only.

In this task instrumentation to measure the vapor pressure of low vapor-pressure, high-temperature materials by means of measuring evaporation rates of these materials in vacuum at elevated temperatures is developed. The method utilizes a piezoelectric quartz crystal, which has a resonant frequency that can be directly related to the sample evaporation rate. The sample temperature is a critical parameter in the measurements. Therefore, design and construction of an automated temperature control system in order to keep the sample temperature constant, is the major component of this work. Vapor pressure data of silver is obtained in order to compare it with the data in the literature and

to demonstrate the validity of the method used in this work.

Accomplishments

During the course of this research project, we have designed and constructed a fully computerized automated temperature control system to be used to measure vapor pressure of high temperature oxide materials. We used an existing high vacuum chamber to house the sample, heating element, and the detector system. Initially, underlining constrains of heat transfer, evaporation rate, and molecular flow concepts were studied and several assumptions were made. A mathematical model of the controller was developed. Based on this theoretical studies, we have designed the sample holder and heat shields which eliminate any radiative heat loss may occur in the system, and implemented the crystal detector system measuring mass loss from the system and thermocouples measuring the temperatures of components in the chamber. The automated controller system is fully functional. The preliminary experiments with a sample whose vapor pressure is in the literature have shown the reliability of the method and the procedures to measure vapor pressure of other materials. However, initial assumptions regarding the heat transfer and efficiency of radiative heating was not met in the experiments. Therefore, we have modified the heat shields so that the heat generated from the heating element be used more efficiently. The sketch of the new heat shield design is shown in Figure 5.

Before the modified heat shields, we were able to heat the sample up to 800 C which is much below the expected operating temperature of 2000 C. Our calculations show that we should be able to get to this desired temperature with the new heat shields. however, due to time constraint in this project we have not obtained any data to confirm the operating temperature range with this new construction. Although, we have not obtained any data on vapor pressure of rare-earth materials, as the result of this research, currently, the Space Power Institute (SPI) of Auburn University has a fully operational facility to be used to measure vapor pressure and determine life expectancy of new advanced materials, and a facility to perform similar experiments to the ones listed above.

Experimental Approach

The key element in this work is the detection of the mass loss from the sample at elevated temperatures. This is measured by using a piezoelectric quartz crystal as the sensor of the detection system. A variable power supply and a tungsten filament foim the heating system for the sample. In thin film deposition technology, crystals are used to measure both the thickness and deposition rate of the film onto a substrate. The technique makes use of the piezoelectric properties of a quartz crystal as a sensor. When a voltage (RF frequency) is applied to a quartz crystal, it oscillates at its natural frequency. When the crystal sensor is placed near the sample, molecules deposited on to the crystal changes its mass, and consequently, its resonant frequency is lowered. Recording these small frequency changes by rapid sampling, the mass rate or deposition rate is recorded as a function of time. The resolution of these detector can be as high as 0.1 A in thickness.

In this work, the detector is located directly above the sample/heating elements assembly at a distance 2.5 cm away from the sample's surface, which is smaller than the estimated mean free path of the molecular flow from the sample while it is heated to elevated temperatures. Tungsten filaments are used as the heating elements and are placed beneath the sample. To ensure uniform temperature across the sample, a thin tungsten plate is located in between the filaments and the sample. Thus the sample is radiatively heated uniformly across its surface. Although radiative heating may not be as efficient as conduction heating, if the conduction heating were used then only the heat at contact points between the sample and the filament would be transferred leading to the non uniform heating of the sample. Additionally, at vacuum conditions good contact cannot be assured. Therefore radiation heating is most preferred in this work. Figure 6 shows the schematics of sample and heating element assembly.

The sample temperature is monitored by several (two in this case) thermocouples which are located at different points on the sample surface. Also, radiation shields are placed beneath the tungsten filaments to reduce radiation loss and reflect radiation back to the tungsten plate. This is shown in Figure 1 including the sample, heating element, and the sensor assembly. This whole assembly is placed in an ultra high vacuum chamber where the pressure is sustained at 10^{-10} torr at room temperature, and at 10^{-8} torr at 200°C ambient (chamber) temperature. The ultra high vacuum chamber was pumped down in two stages: first it was pre-pumped by sorption pumps up to 10^{-2} torr pressure ranges, and then it was continued to be pumped by a cryogenic pump until the pressure reached to 10^{-10} torr ranges. The pumping procedure usually takes 1 to 2 weeks of time depending on the environmental factors at the time of placing the sample in the chamber. Figure 7 shows the vacuum system used to conduct the experiments, and Figure 9 illustrates the schematics of the complete system including diagnostics and data acquisition equipment.

Automated Temperature Controller and Computerized Data Acquisition

Because the mass loss rate data is highly dependent on the temperature of the sample, it must be precisely controlled during the experiment and must be kept at constant values during each data point. Therefore much of the efforts concentrated on design and construction of an automated temperature controller system. Further, this temperature controller was controlled by computer. This same computer was also used to collect the data from the system and provided the reference voltage to the power supply heating the filament.

Initially a mathematical model based on "system identification" technique was developed to design the automated controller. System identification technique simply involves a procedure of inputting a known signal into the system and measuring the output from the system. In our design, the input to the system is the voltage supplied by the power supply to the heating element, and the output is the temperature of the sample being heated and measured by thermocouple located on the surface of the sample. There are several system identification methods in the literature, however, two of these, namely least squares and non-negative least squares, were examined to determine the best suitable one in this

work. Further, each of these involves a solving a system of set of equations for a set of parameters. After determining the set of equations describing the system, we examined several possible feedback control systems including "proportional plus integral plus derivative" (PD), "proportional plus integral" (P1), and "H- infinity", to implement the best possible one to the design of the automated controller. Each of these control systems must be linear, time-invariant, and stable limiting the large voltage swings which may occur during voltage changes (step-up) to increase the temperature of the sample to measure the next evaporation rate data point. The main reason for this limitation is to avoid any damage to the heating element and to the *DIA* boards on the computer during this short time voltage overloads. The next constraint on the design is the temperature of the crystal sensor. Although the sensor is water cooled, because it is very close to the sample, its temperature may reach to levels higher than 400 C which is the upper operating limit of the sensor. Therefore, we have placed a thermocouple to monitor the sensor temperature and this measured parameter was also coupled into sample the equations identifying the system as one of the system identification parameter.

A computer interface system including a *DIA* converter, an IEEE-488 controller board, and an AID converter in addition to a "C" computer program and "Labtech Notebook ProTM" data acquisition software packages was used to collect the data from the system. The collected data included the temperature data measured from the sample, mass loss (which is in fact mass gain on the sensor) data measured by the sensor, temperature of the crystal sensor housing, and the wall temperature (which is the background temperature) of the chamber. The AID board receives a voltage (which is the temperature data of respected components) from the thermocouples and converts it to a digital signal where the software can display it on screen and save it to a file at the same time. The *DIA* board receives a signal from the computer and converts it to an analog signal that is the voltage used as the reference voltage for the power supply. The IEEE-488 received data which includes the thickness of the film deposited on the crystal sensor, the rate at which the film is deposited on the sensor, the elapsed time since the experiment began, and the life of the sensor, from the crystal deposition sensor through a deposition monitor.

The Labtech data acquisition package was used for controlling the system as well as data collection and data manipulation. The closed loop structure of control system used in the experiments is shown in Figure 8, and the data for the system identification experiment are displayed is Figure 10.

Vapor Pressure Measurements

When the sample begins to heat up, the surface molecules evaporated and propagate towards the cooler regions in the chamber. Since the crystal sensor is located just above the heated sample, and it is kept at much cooler temperatures than the sample, the molecules leaving the sample's surface stick to the surface of the detector and add mass to the crystal. This mass increase lowers the resonant frequency of the crystal. Therefore, the mass flow rate from the sample is measured by measuring this small change in frequency over time. Once, the mass flow rate is measured, the evaporation rate of the material can

be calculated.

Although, the aim of this research is to measure vapor pressure of rare-earth oxides and high temperature low vapor pressure materials, we used a silver sample as the "test sample" to demonstrate the validity of our design and the method used in this research. Figures 11-13 shows a representative mass flow data of silver. We determined the vapor pressure of silver for given temperatures and found that the values obtained in our experiment are very close to the ones in the literature.

Future Work

The Space Power Institute (SPI) of Auburn University has a fully operational facility including an ultra high vacuum chamber with a cryogenic pump, an automated temperature control system, diagnostic equipment and a computerized data acquisition system for measuring vapor pressure and determining life expectancy of high temperature materials. Currently, we have a new heat shield system on the sample holder and our calculations show that we will be able to reach the temperature range of 2000 Centigrade with this new construction. However, we have not run the system after this modification to see if the data can be obtained at this temperature. We are confident that, if funding and time were available to us to continue this project, the facility would perform as designed.

Degrees Awarded and Undergraduate Students worked on the Project

John Ingram, MS candidate in EE has finished the theoretical and experimental parts of his research. Expected graduation is Winter '99 Quarter.

Three undergraduate students worked at various times on the project as part of technical electives courses.

Publications

J. Ingram, A. S. Hodel, and H. Kirkici, "Robust Temperature Control in the Measurement of High Temperature Vapor Pressures," in the Proceedings of the IEEE 1997 Industrial Electronics Conference, November, 1997, New Orleans, LA.

Hulya Kirkici, John Ingram, and Scott Hodel, "Evaporation Rate Measurements of Low Vapor-Pressure, High-Temperature Materials: Experimental Studies and Instrumentation" in preparation, to be submitted to the *IEEE Transactions on Instrumentation*, December 1998.

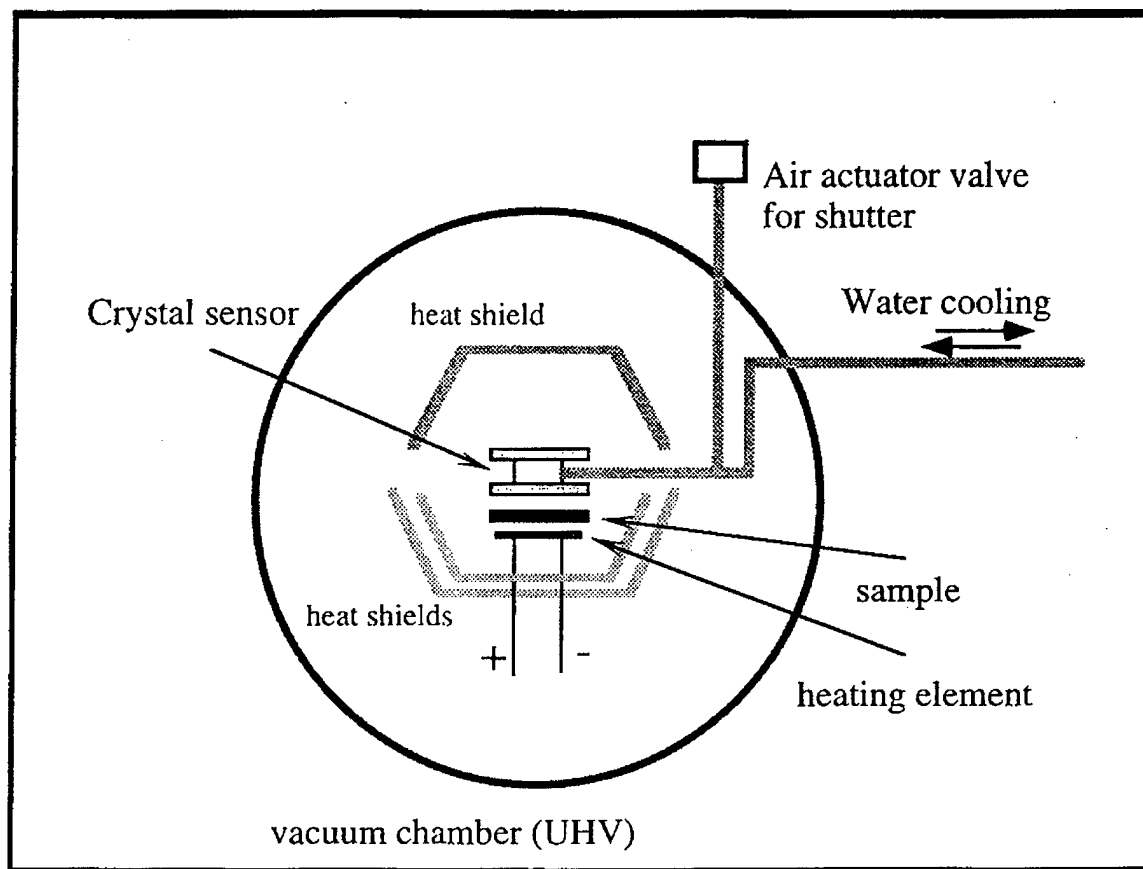


Figure 5. Diagram of the Sample Holder, Detector, and Vacuum Chamber.

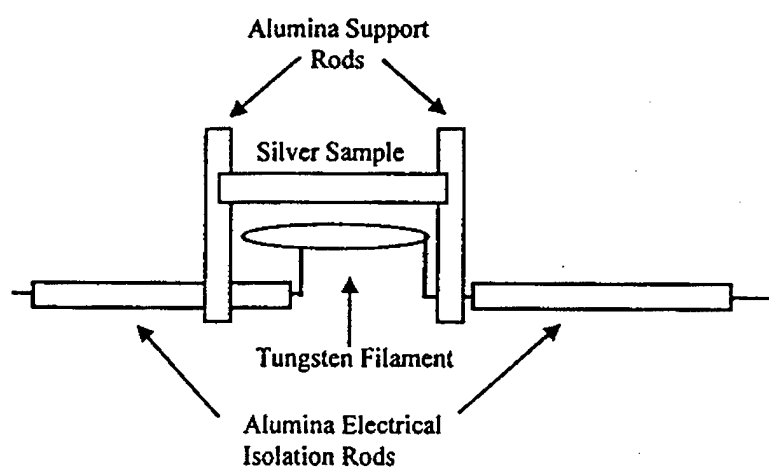


Figure 6. Diagram of the Sample and the Heating Element Assembly.

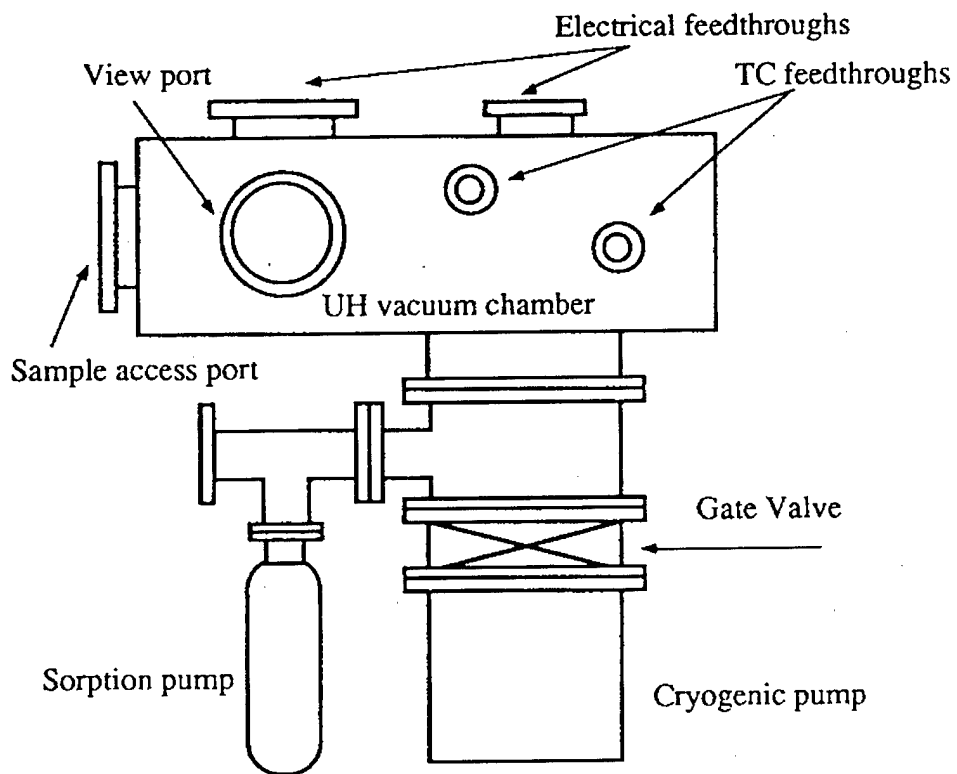


Figure 7. Vacuum System used in the Experiments.

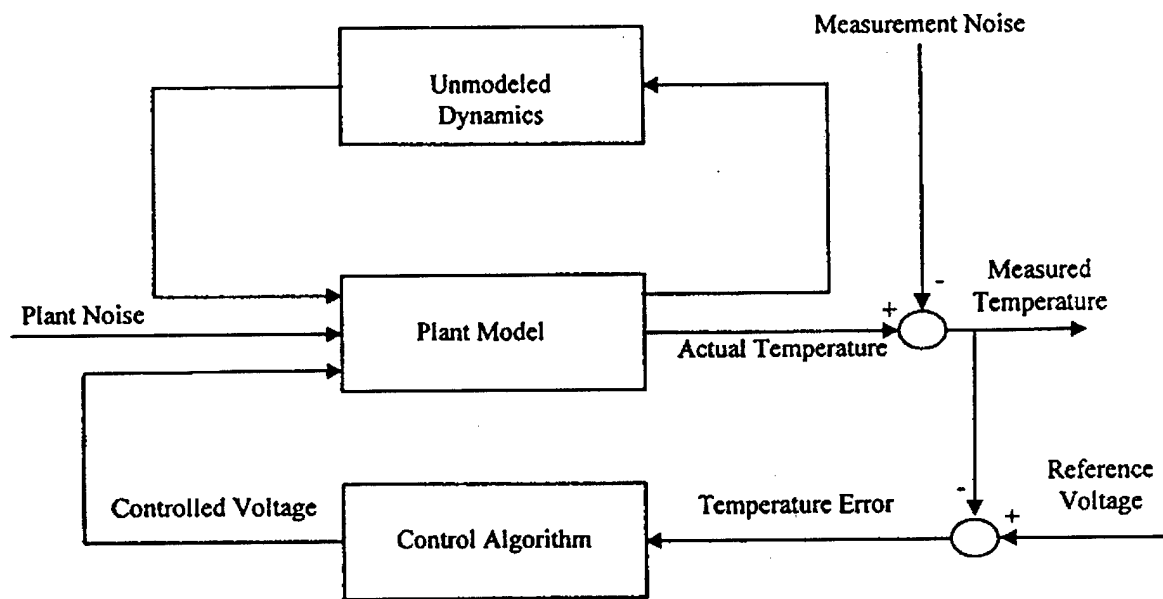


Figure 8. Closed Loop Structure of the Control System.

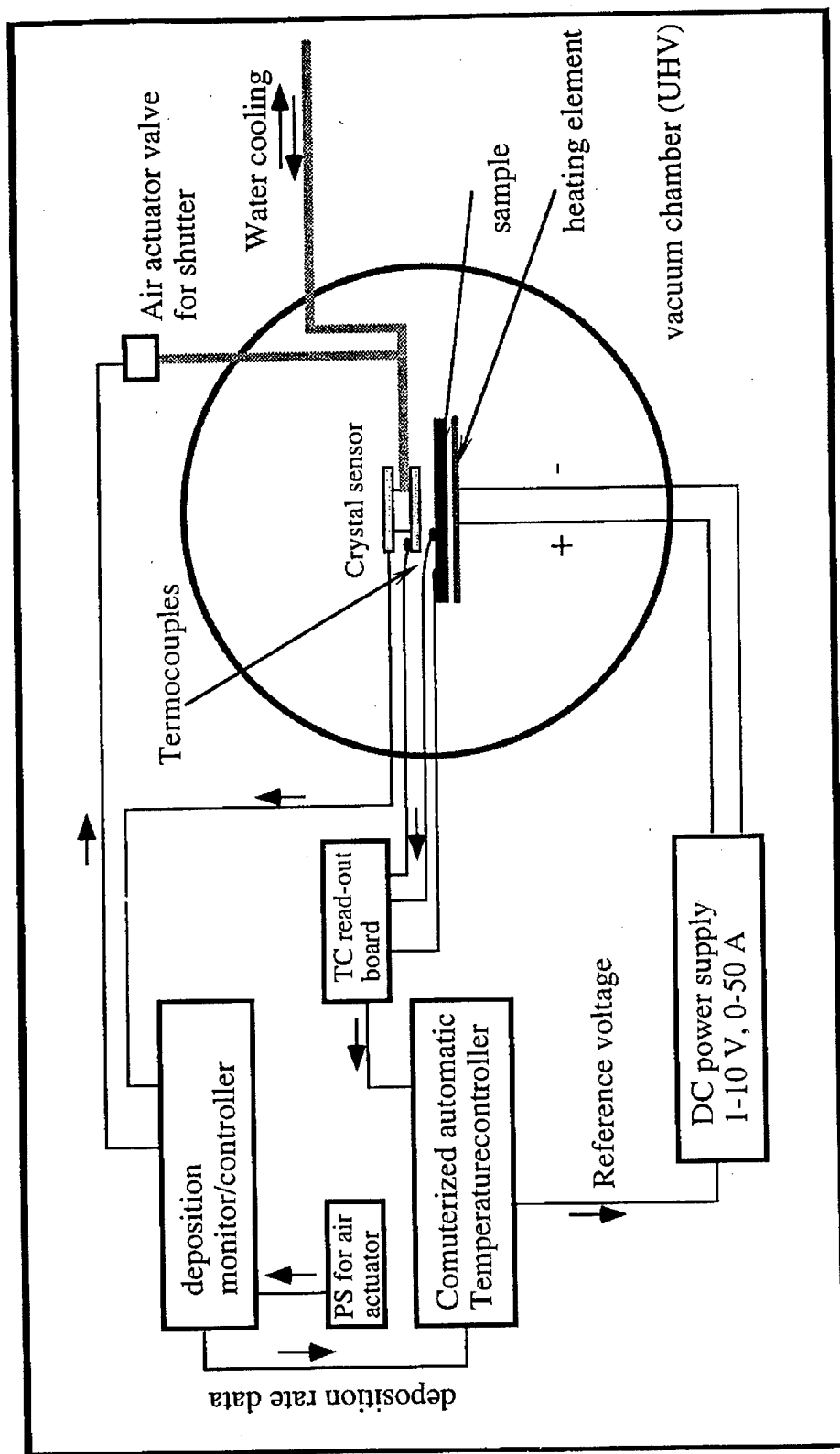


Figure 9 Schematic of the Complete System.

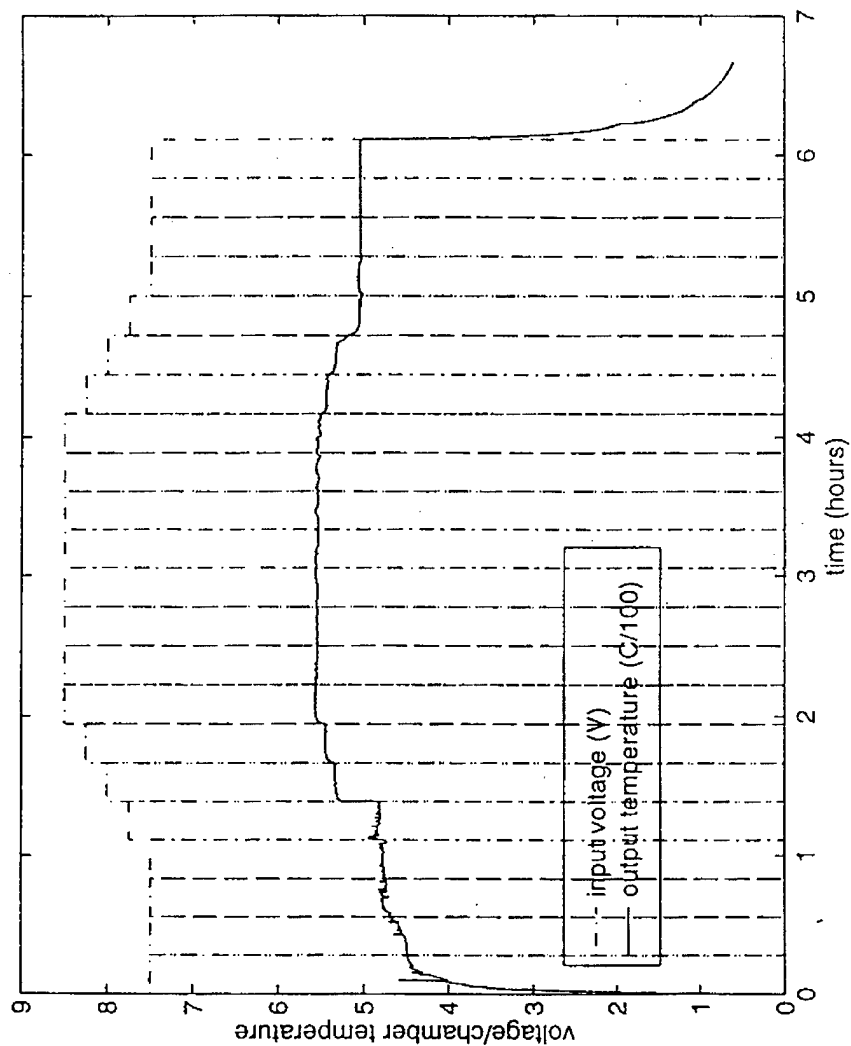


Figure 10 Data for the system identification experiment showing the input voltage to the filament, and recorded output temperature of the sample.

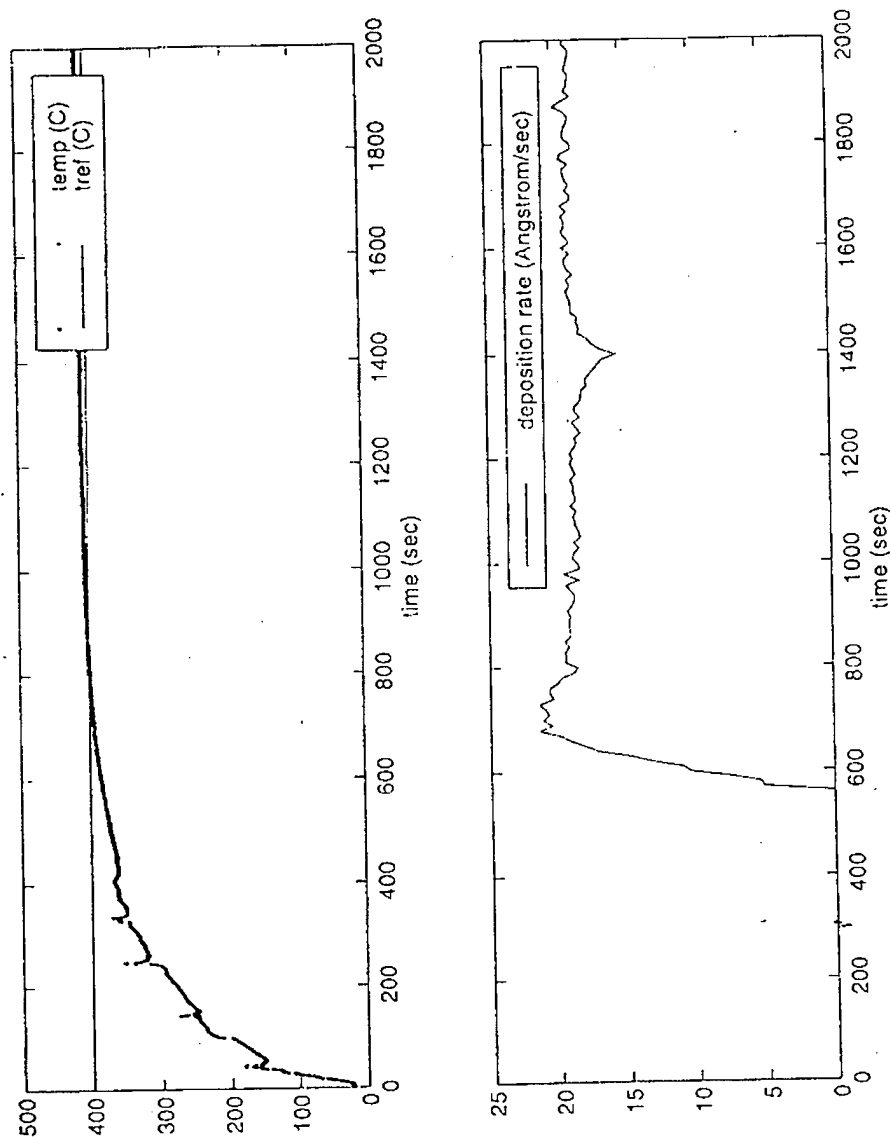


Figure 11 Vapor pressure measurement with the automated controller. The total "run" time of the experiment is 6000 s (approximately 1 h 40 mm.). (a.) The reference voltage and sample temperature as a function of time. (b.) The deposition rate measured in angstroms by the crystal sensor. (this figure cover from $t = 0$ to $t = 2000s$)

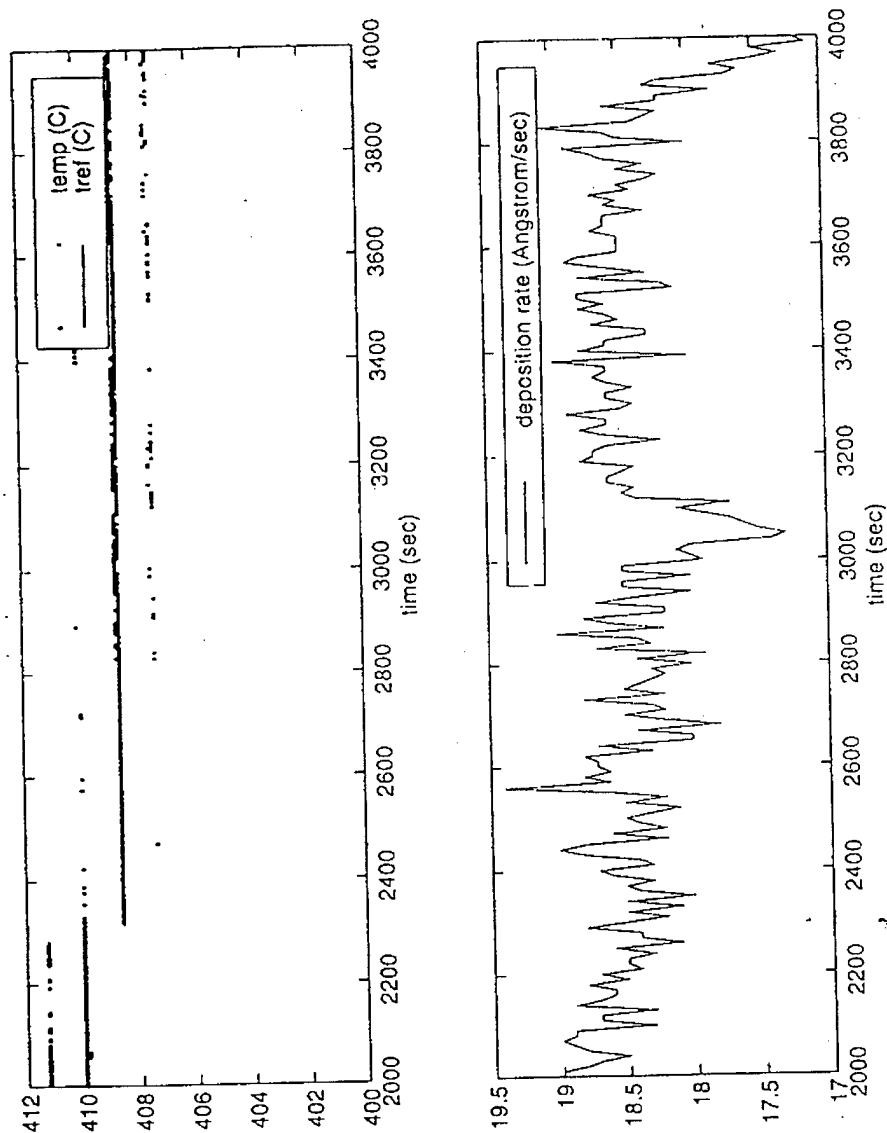


Figure 12 Vapor pressure measurement with the automated controller. The total "run" time of the experiment is 6000 s (approximately 1 h 40 mm.). (a.) The reference voltage and sample temperature as a function of time. (b.) The deposition rate measured in angstroms/s by the crystal sensor. (figure covers from $t = 2000$ to $t = 4000$ s)

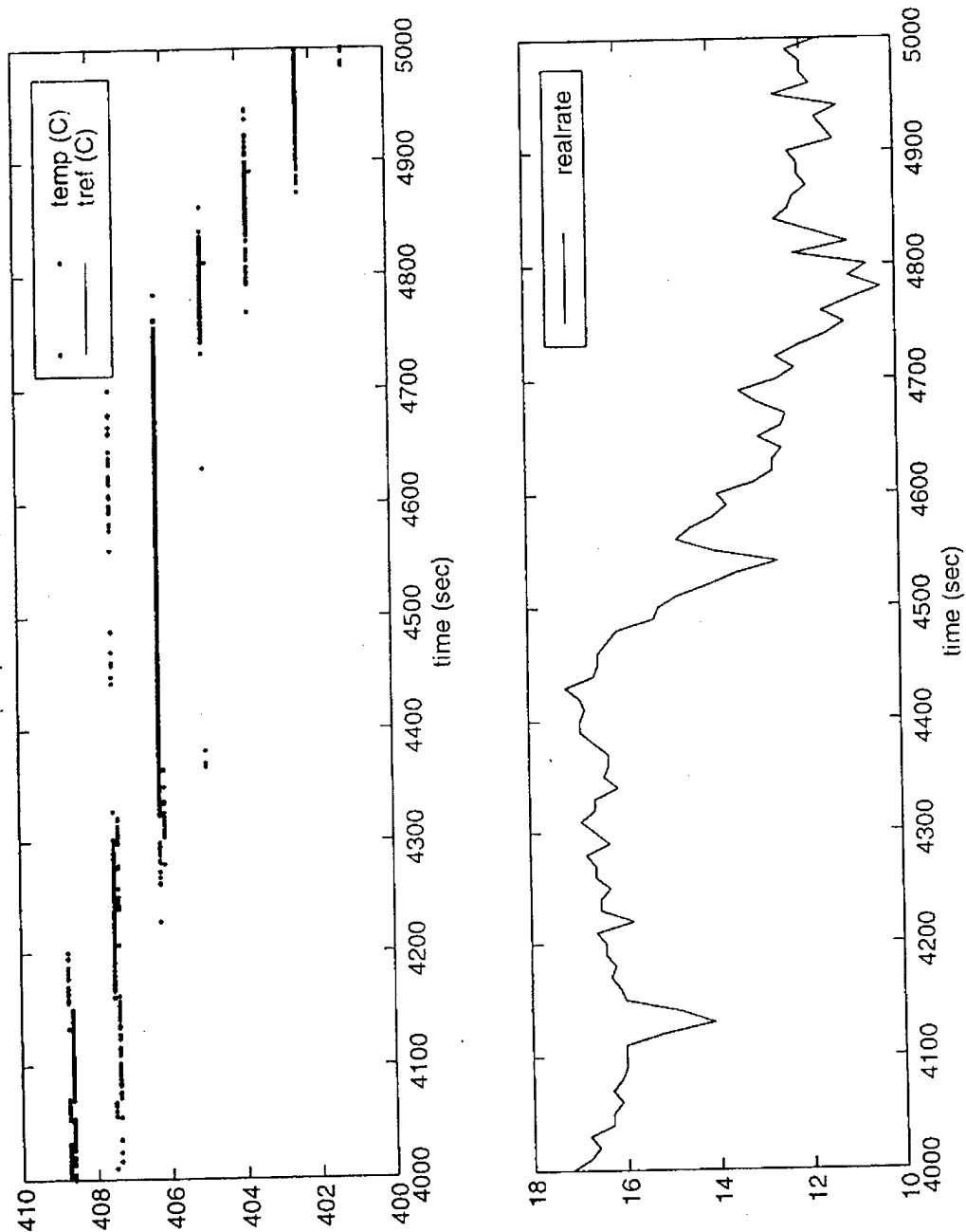


Figure 13 Vapor pressure measurement with the automated controller. The total "run" time of the experiment is 6000 s (approximately 1 h 40 mm.). (a.) The reference voltage and sample temperature as a function of time. (b.) The deposition rate measured in angstroms per second by the crystal sensor. (figure cover from $t = 4000$ to $t = 5000$ s)

SUMMARY

This program has been an enormous success when viewed from the technology introduced into the R&D infrastructure. Fiber strengthening and selective emission were championed as the best way to develop thermophotovoltaic systems. At present most, if not all, of the current systems approaches to TPV employ selective emission and some form of strengthening at high temperatures. The technical impact has been substantial both in terms of technology and people. A summary of the quantifiable results from this research project is given below:

• Technical papers/conference proceedings	38
• Masters of Science theses	6
• Doctor of Philosophy theses	4
• Post Doctoral Fellows	7
• Undergraduate student assistants	6
• Patents issued	3