LA-UR - 78-1149

CONF-780447--1

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SUBMITTED TO: Talk and paper to be given at the Solar Thermal Test Facilities Users Association Annual Meeting, April 11, & 12, 1978.

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CONTRACT W-7405-ENG. 36

NIGHT STORAGE AND BACKUP GENERATION WITH ELECTROCHEMICAL ENGINES*

by

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ABSTRACT

Li/I_2 electrochemical engines both store and generate electric power. These dual capabilities complement solar photovoltaic generation in critical areas: Photovoltaics need backup storage at least for nights and, if possible, for two or three days' needs. Such storage must be relatively cheap and compact--aqueous batteries would have trouble filling these requirements. Likewise, photovoltaics need backup generation based on combustion of fossil fuels for periods of bad weather -- solar residences or communities will probably have to supply their own backup generation because central generating stations cannot be expected to keep large amounts of equipment on standby for solar users.

This paper describes Li/I_2 engine designs which could be developed to fill these needs of solar users, i.e., storing electricity generated by photovoltaics and generating additional electricity from fossil fuels as needed. Calculations based on laboratory performance indicate that the devices could be simple to manufacture, economically competitive, and efficient both in storage and generation.

These engines also could directly use solar energy from focused and tracking solar collectors, or they could indirectly use solar energy through the combustion of biomass materials.

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*This work was supported by the U. S. Department of Energy.

Night Storage and Backup Generation with Electrochemical Engines

Guy R. B. Elliott
and
N. E. Vanderborgh

INTRODUCTION

Practical photovoltaic conversion systems will have to be used in association with devices which generate power during periods of low solar flux and which store power for nighttime use. No satisfactory devices of either type are now available for solar homes or for solar communities.

The lithium/iodine electrochemical engines of this presentation do offer both functions in a single, simple device. These electrochemical engines can efficiently generate power over a temperature gradient of roughly 350°C (625K) to ambient, and they can operate with less efficiency from 200°C (475K) to ambient. These same engines can (by simple and rapid switching operations) be converted into efficient molten-salt batteries which operate in the temperature range above. As such they have large storage capacities and can be charged by external electric power sources.

For generator operations during periods of bad weather or when power usage is especially heavy and extra power is needed, electrochemical engines would typically burn fossil fuels (gas, butane, fuel oil, etc.) to maintain the temperature gradient necessary to convert heat to electrical power.

The electrochemical engines offer two other approaches to the generation of electrical power based on solar energy--they could be heated by focused direct solar energy, or they could be heated by combustion of biomass materials which come from sunlight.

ORGANIZATION OF THIS PAPER

We first describe briefly how electrochemical engines act to convert heat energy to electrical energy. Next we discuss laboratory performance of electrochemical engines based on the Li/I_2 chemical system. Finally we calculate expected performance of particular Li/I_2 electrochemical engines used for storage and for each solar-to-electric conversion path mentioned above.

THE CONCEPT OF ELECTROCHEMICAL ENGINES

The driving force of electrochemical engines is the pressure dependence of gas-phase reactions. This dependence is described closely by mass action relationships. Thus for a general Reaction 1A in which liquid A reacts with gas B to form a liquid C, or its reverse Reaction 1B,

$$A_{(l)} + B_{(g)} = C_{(l)} \tag{1A}$$

$$C_{(l)} = A_{(l)} + B_{(g)} \tag{1B}$$

a high pressure of $B_{(g)}$ will favor Reaction 1A while a low pressure of $B_{(g)}$ will favor Reaction 1B.

Electrochemical engines use such reactions as the net electrochemical steps in cells of high temperature batteries. The cells are discharged by Reaction 1A at a high pressure of $B_{(g)}$, and they are charged by Reaction 1B at low pressure of $B_{(g)}$. The pressure of $B_{(g)}$ is controlled by the temperature of an independently heated condenser in which $B_{(g)}$ can be removed from or supplied to the cell region.

Lithium/Iodine Electrochemical System

If the reaction

$$2Li_{(l)} + I_{2(g)} = 2LiI_{(l)} \tag{2}$$

takes place in an electrochemical cell, the Gibbs free energy, ΔG, of the process can be extracted as maximum electrochemical work. At a temperature where I_2 is volatile, the free energy and the voltage ε will be given by

$$\Delta G = -nF\varepsilon = \Delta G^\circ - RT \ln (f_{I_2}/f^\circ_{I_2})$$

$$= \Delta G^\circ - RT \ln P_{I_2} \tag{3}$$

where the gas fugacity, f, is assumed equal to pressure, P, and where the reference fugacities are for 1 atm of iodine and for the condensed phases of the other reactants and products.

Figure 1 shows a schematic drawing of a cell which could be used to carry out the lithium/iodine reaction. Such prototype cells are in laboratory studies.

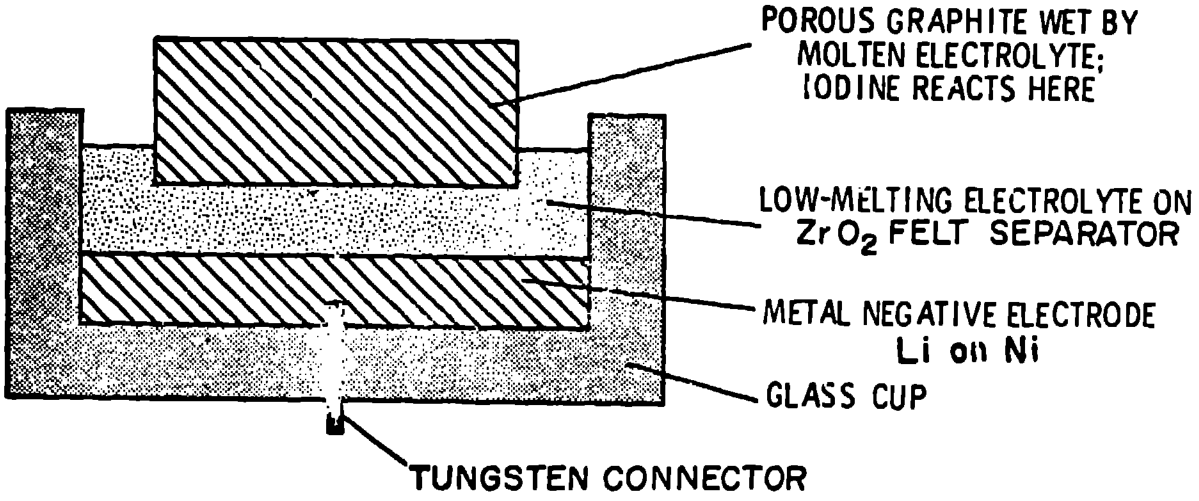


Fig. 1: Laboratory cell of lithium/iodine electrochemical engine.

In the figure a Pyrex cup with tungsten electrical connector holds three layers of material. The top layer is a porous-graphite disk on which the iodine reacts. The middle layer is a porous insulator of zirconia felt; this felt supports the graphite disk and rests on a bottom layer of porous nickel felt wet with molten lithium. A molten electrolyte containing LiI (plus other salts to lower its melting point) wets into void spaces in all three layers -- the lower layers are filled with electrolyte, and electrolyte partially fills the porous graphite by capillary action.

Electric power can be supplied by the cell by connections to the lithium-nickel felt-tungsten rod (negative electrode) and to the iodine-porous graphite electrode (positive electrode). The open circuit (no-drain) voltage of such a cell is calculable from thermodynamic data as in Eq. 3. Values for ΔG° at elevated temperatures are available from the JANAF Tables.

For a pressure of 1 atm of I_2 and a cell temperature of 625 K

$$-46{,}122\ \varepsilon_{(1\ \mathrm{atm})} = -121{,}800 - 4.575\ (625)\ \log 1$$

$$\varepsilon_{(1\ \mathrm{atm})} = 2.64 \text{ volts} \qquad (4)$$

For 20 atm (v.p. of I_2 at 625 K)

$$\varepsilon_{(20\ \mathrm{atm})} = 2.72 \text{ volts} \qquad (5)$$

and for 0.000405 atm (v.p. of I_2 at room temperature)

$$\varepsilon_{(0.000405\ \mathrm{atm})} = 2.43 \text{ volts} \qquad (6)$$

Laboratory Li/I_2 Electrochemical Engines

If cells are stacked and sealed into two evacuated, Pyrex, cell-stack units as shown in Fig. 2, then an electrochemical engine is formed. Here two identical cell-stack units are placed in electrical opposition by joining the positive junction of one unit to the positive junction of the other unit. Power can be drawn from the two negative leads if one condenser is cooled.

If the temperature in both condensers is the same, no net voltage is developed across the negative electrodes and no current flows. The individual (and opposing) voltages are given above. For T_1 = 625K the opposing emfs are 2.72 volts (Eq. 5) per cell or 16.32 volts per cell-stack unit for these conditions.

If one condenser is cooled to T_2 = 298 K, the pressure of iodine vapor in that unit will drop to 4.05×10^{-4} atm, and the emf will be 2.43 volts (Eq. 6) per cell or 14.58 volts from the cell-stack unit.

At this point the two units act as an electrochemical heat engine. As current flows, one unit is discharged and the other is charged. The net reaction per two Faradays of electricity generated is

$I_2(P_1,T_1$, hi T condenser) → $I_2(P_2,T_2$, lo T condenser)
Li(side of hi T condenser) → Li(side of lo T condenser)
LiI(side of lo T condenser) → LiI(side of hi T condenser)
[illegible]

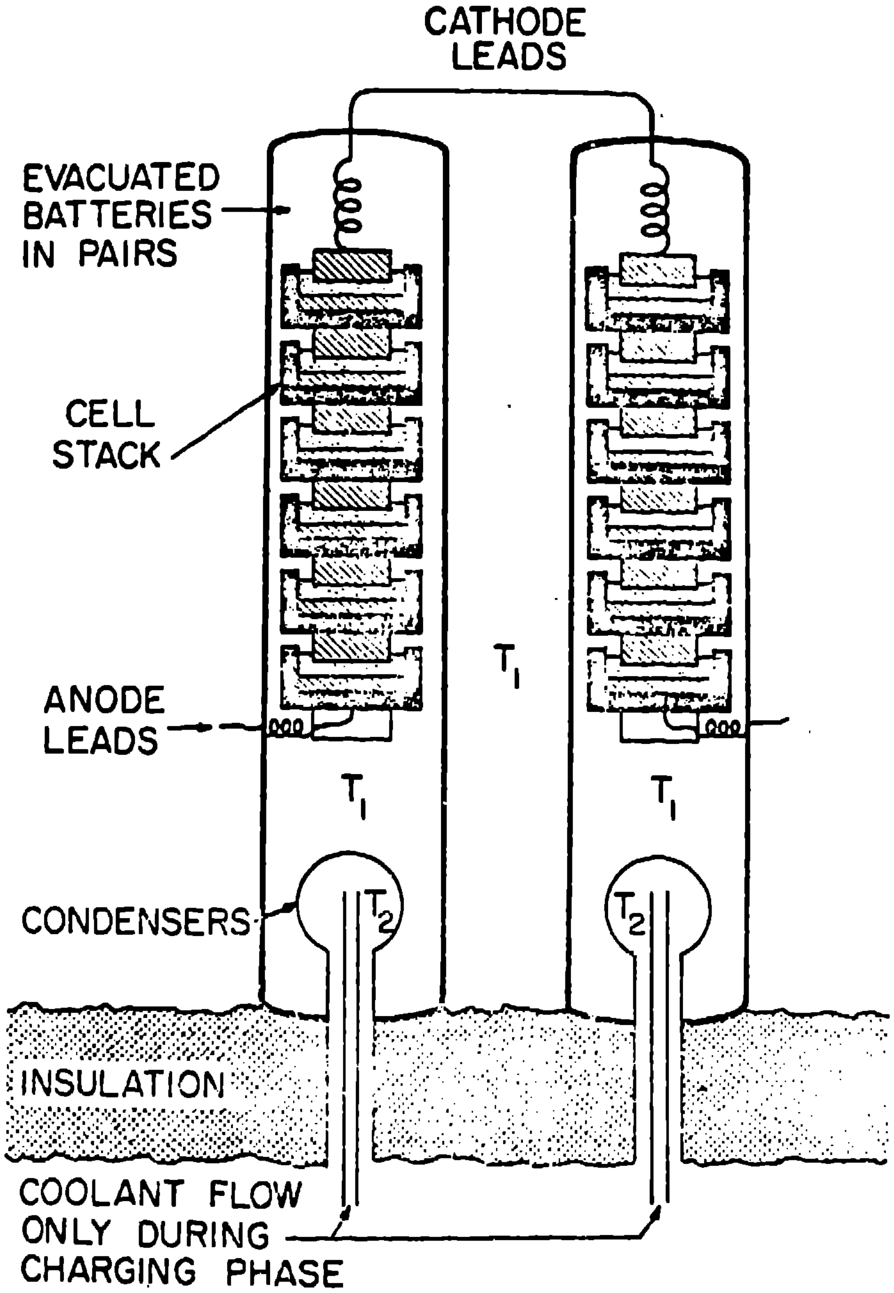


Fig. 2. Laboratory electrochemical engine with two cell-stack units of six cells each.

At very low drain the net emf will be 2.72-2.43 = 0.29 volts per cell pair or 16.32-14.58 = 1.74 volts from the two units which make up one electrochemical engine.

The electrochemical engine cycle starts with one fully charged cell-stack unit with (condenser) T_2 = 625 K and one fully discharged unit with T_2 = 298 K. Then, when the high voltage side has completely discharged, the low voltage side is completely charged. At this point the cold condenser is heated, the hot condenser is cooled, and current flows in the opposite direction (requiring an external switching to maintain the proper current direction). At the end of two such half cycles, the engine will be in its initial state, but net conversions of heat to electrical energy will have been accomplished.

(This behavior is consistent with Carnot limitations--the ΔH of vaporization of I_2 is supplied at the high temperature and the ΔH of condensation is discharged at low temperature, and this limits the efficiency of conversion.)

In addition to generating electric power, these cell-stack units can (by breaking the electrical connection between the two-cell stack units) each be used separately as an energy storage device. The voltage required to charge such a storage device is greater than 2.72 volts times the number of cells in a stack.

Experimental Behavior of Li/I_2 Electrochemical Cells and Engines

The experimental behavior of prototype cells using lithium and iodine with a molten electrolyte containing LiI is consistent with the theory mentioned earlier. Voltages in Eqs. 4 and 6 are found experimentally.

Experimental Li/I_2 cells have shown very small internal resistances, as low as 0.8 ohm/cm^2. Internal resistances are constant over wide current densities from 0.25 amps/cm^2 drain to 0.80 amps/cm^2 of charge. Such remarkable behavior could only be found in fused salt solutions.

On the basis of thermodynamics and the experimental performance, one can calculate the expected performance from commercially scaled models of these Li/I_2 electrochemical engines. Such estimates conclude this paper.

A POSTULATED COMMERCIAL Li/I_2 ELECTROCHEMICAL ENGINE

The Cell Design

Fig. 3 is a promising cell design suitable for mass production. Five different types of solid parts of the cell are shown. Electrolyte will be added after assembly into cell-stack units; the liquid and gaseous cell reactants will be formed at the generating station by electrolysis. Consequently handling of potentially hazardous chemicals (lithium metal and molecular iodine) will be eliminated.

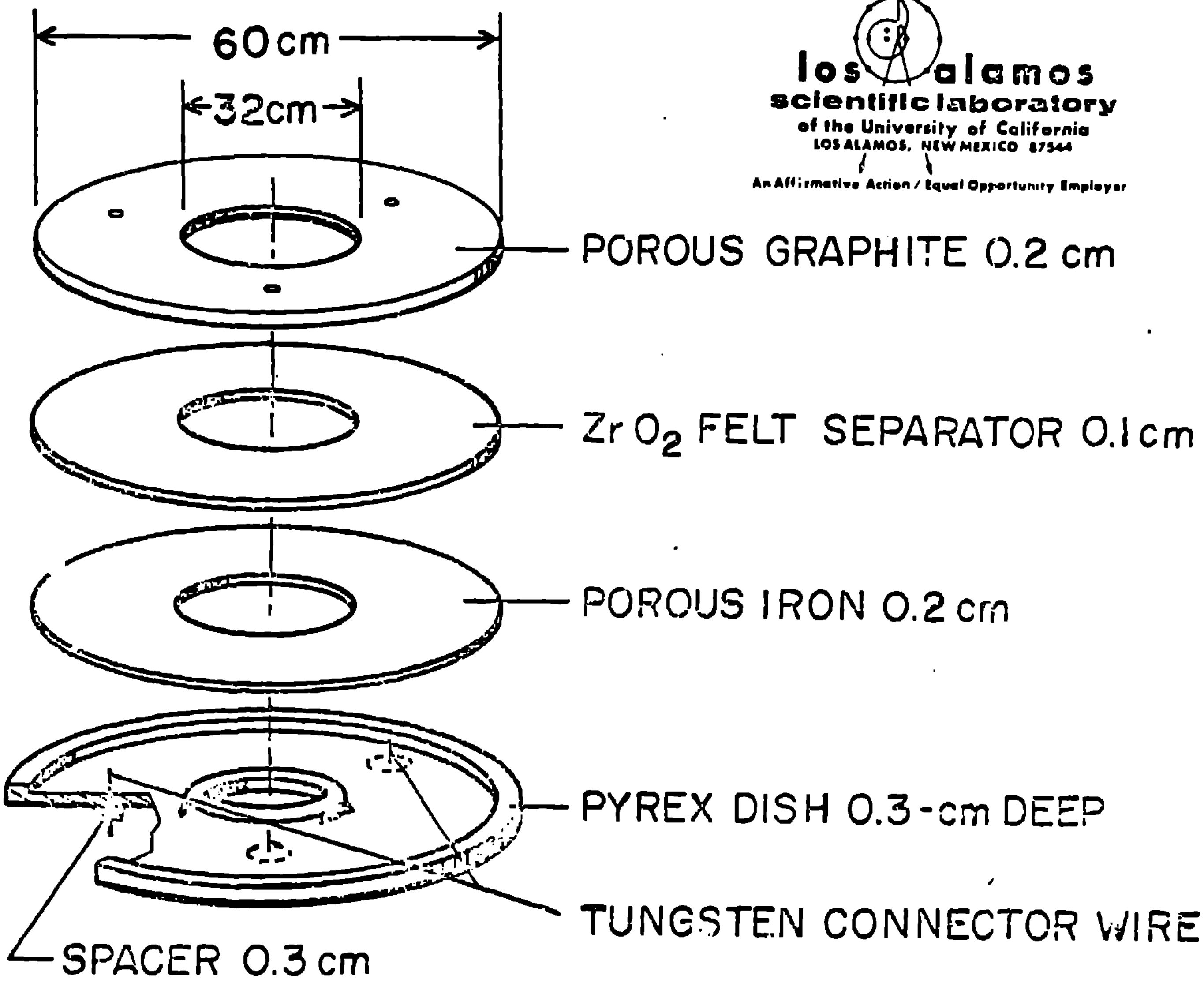


Fig. 3: Postulated commercial design of Li/I_2 electrochemical engine cells.

The top thin disk of porous graphite serves as the positive electrode. It has large electrode surface area, and it is thin to provide rapid iodine transport. This porous graphite has two sharply different pore-size ranges, thereby allowing capillary action to wet the electrode like a half-filled sponge. Because of the partial filling and different pore sizes, the same region of the cell has continuous paths for vapor movement, for electrolyte conduction, and for electronic conduction (graphite).

Next is the separator. ZrO_2 felt is indicated, but other materials may do as well. We find ZrO_2 is not significantly attacked by metallic lithium.

Below the separator is the negative current collector. This porous metal disk transports electrons. At present the current collector is made from sintered iron. Perhaps nickel coating to improve the wetting characteristics by the lithium will be necessary.

At the bottom are additional solid parts, a Pyrex cup and tungsten connector wires. The Pyrex cup holds the cell components and acts as a liquid electrolyte reservoir. The tungsten connector wires (tungsten is not corroded by iodine vapor) serve two purposes: First, they connect the negative electrode of one cell to the positive electrode of the next cell below in the stack. Second, they act as spacers to maintain unrestricted vapor transport.

These cells have an area of 2000 cm^2, an OD of 60 cm, an ID of 32 cm, and a thickness of 1.5 cm, including the spacers. The hole is included for heat-transfer purposes.

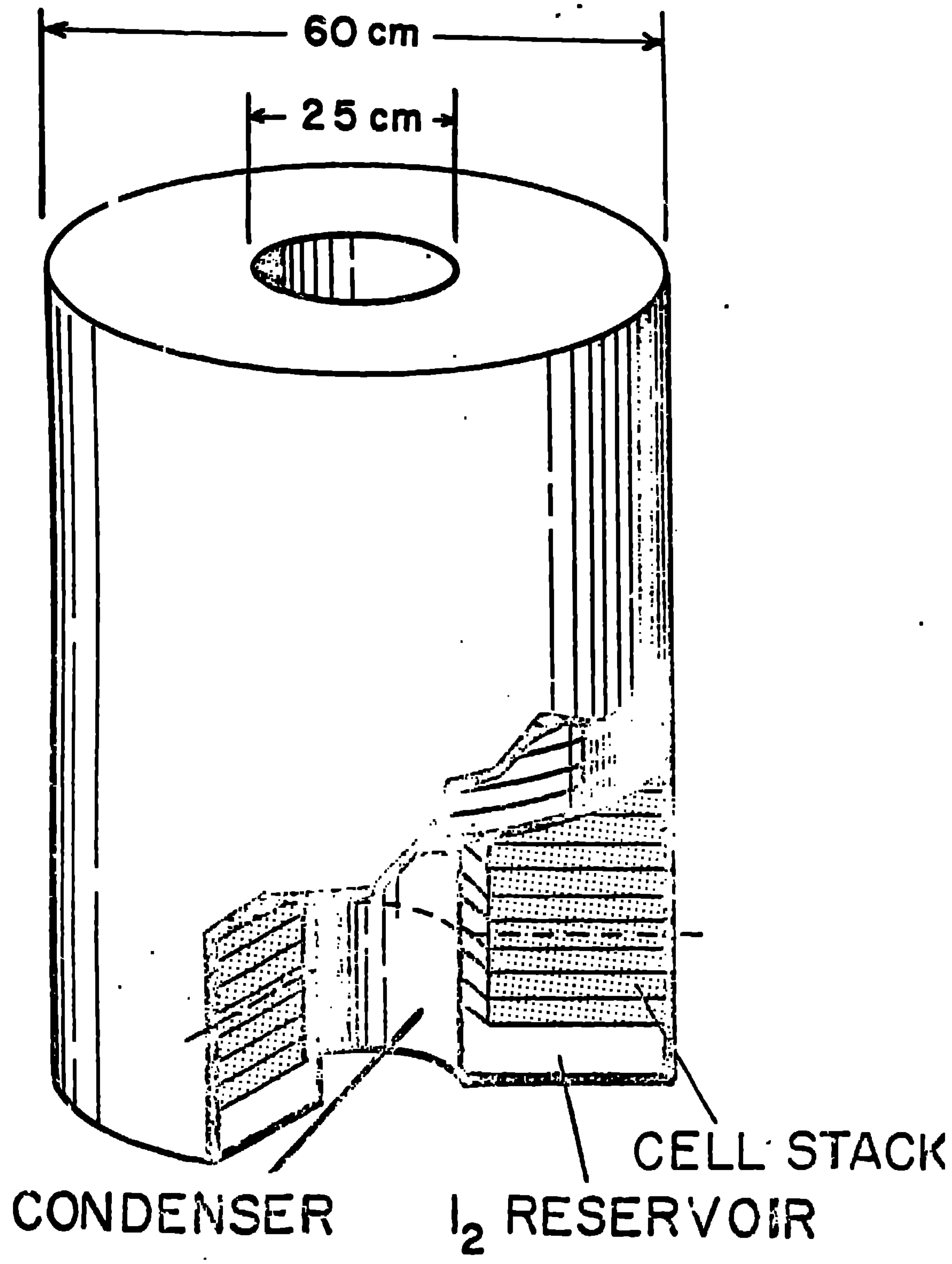
One hundred cells are stacked in a double cylindrical container made from protected steel. The cells touch the outer cylinder, but the inside cylinder (25-cm OD) is smaller than the holes in the cells. This construction allows heat to be supplied to the outside region while the inside region is cooled by air flow and serves as a condenser, and the space between the cells and the condenser presents unrestricted vapor paths. An open region below the cells serves as the I_2 reservoir.

When the construction of the cell-stack unit is essentially complete, the unit is dipped into a bath of molten electrolyte, then drained, thereby filling the cells with electrolyte. Finally, the cell-stack units are evacuated and sealed.

Once sealed, a cell-stack unit is not opened again.

The Cell-Stack Unit

Fig. 4 shows a cell-stack unit design.



electrically separated to act solely as a storage battery if that were desired.)

The Li/I_2 Electrochemical Engine Design

Fig. 5 shows our concept for the electrochemical engine design which will be useful with solar power. The device shown is one cell-stack unit installed in its insulating cover with provision for the heating and cooling necessary for operation. Two such units are needed for one electrochemical engine, see above.

Storage

For electrical storage, both fans are off, both vent doors are closed,and heat is supplied to maintain the operating temperature. We assume a temperature of 625K for the storage operation.

The calculated storage efficiency is high. For a 100-cell unit which drained 40 amps through 2000-cm^2 cells at 272 volts open circuit with a specific resistance of 0.8 ohm-cm^2, the internal voltage drop would be 100(40/2000)(0.8) = 1.6 volts. Even if we allow for concentration polarization during both charging and discharging and for limited self-discharge, the actual storage efficiency should still be over 95%.

The unit can store 40 KWH of electrical energy with a change of less than 1 mm in the depth of the electrolyte in the cells.

Generation

For generator operation one unit is maintained at 625K throughout by externally supplied heat. This is the discharge unit. The second unit will be heated more strongly to maintain the temperature while the unit does electrochemical work as charging occurs. Here the fan will circulate cooling air (cooled by a water wick in summer) through the condenser with the vent door open.

At small drains the discharging unit will generate 100(2.72) = 272 volts, and the charging unit will require 100(2.43) = 243 volts. A net gain of 272-243 = 29 volts is available to do external work.

Allowing for the specific internal resistance of 0.8 ohm-cm^2, and draining 50 amps through 2000 cm^2 in each of 200 cells will reduce the 29 volts by 0.8(50/2000) = 0.02 volts per cell or 4 volts overall. In addition there will be some concentration polarization over what we measured in our experiments (which were for short terms) as the cells are charging or discharging. Our present experimental data do not allow us to calculate this effect accurately, but it is probably adequate to estimate this loss [illegible] small.

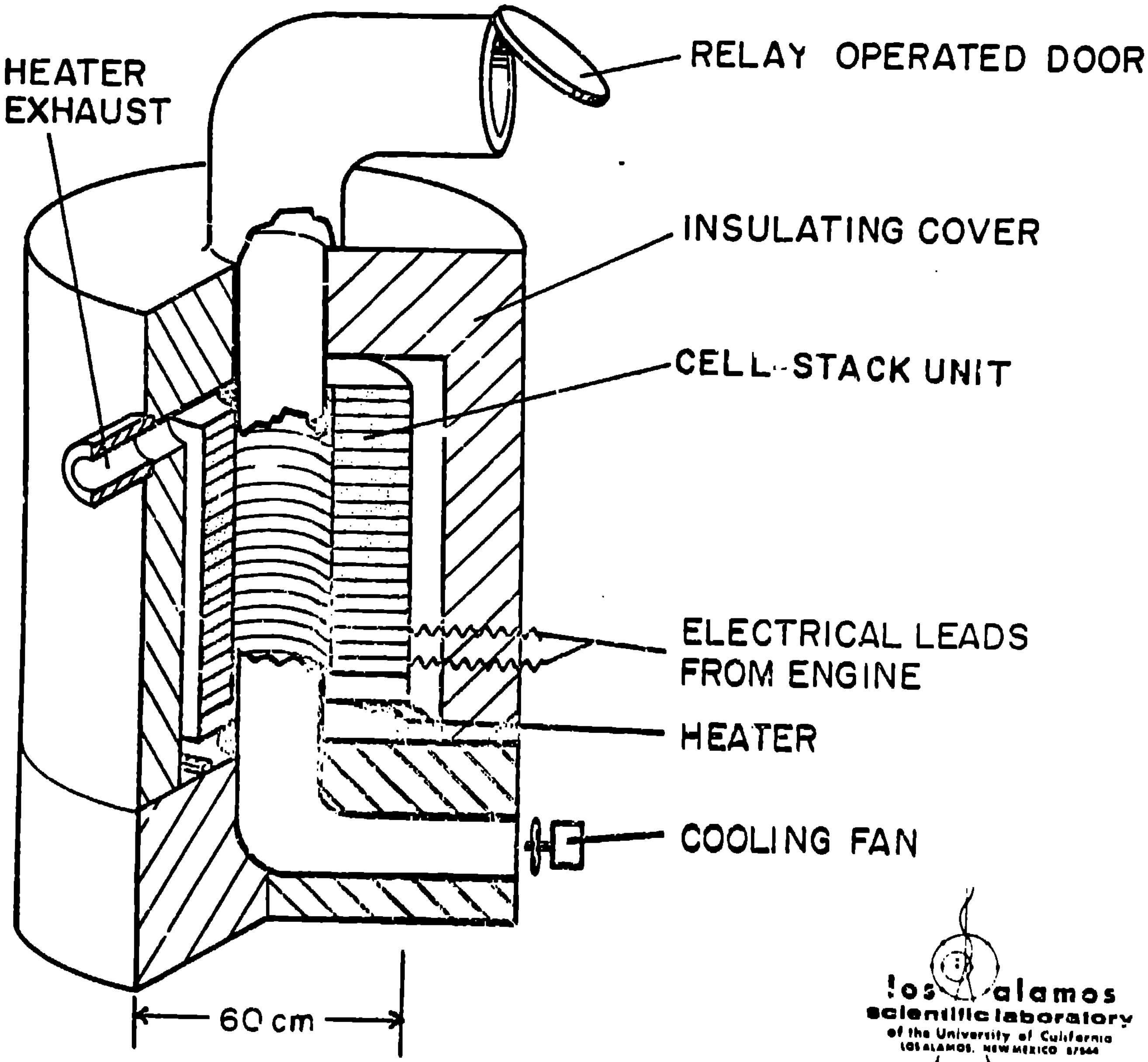


Fig. 5: Li/I_2 Electrochemical Engine Unit. (At least two used together.)

This method of operation would produce 50(29-4-4) = 1.1 KW or 25 KWH per day. Considering the Carnot efficiency (625-300)/625 = 52%, the internal resistance and concentration effects (29-4-4)/29 = 72%, and the portion of the heat of air combustion of natural gas which can be delivered at 625K, i.e., 85%, leads to a very respectable energy conversion figure of 32% for gas heat of combustion to electric power at the busbar.

If more rapid power generation were required, the unit could put out 1.3 KW at a lowered efficiency of around 26%.

With more than two-days' worth of energy generation stored in one cell-stack unit, the charging-discharging roles of the two cell-stack units need switching only after about two days. To supply power during switching periods, and to level the home power usage load, an additional battery would undoubtedly be installed parallel to the home usage load. The load-leveling batteries could be incorporated as sections of the electrochemical engine's cell stacks and are not discussed additionally.

THE USE OF ELECTROCHEMICAL ENGINES WITH PHOTOVOLTAICS

Perhaps the most ideal combination for solar-powered electricity generation is photovoltaics and electrochemical engines. Here the photovoltaics operate in diffuse or direct sunlight, and the electrochemical engines supply the needed storage and backup generation.

The present electrochemical engine design allows storage of 80 KWH total in the two cell-stack units. This 80 KWH is four-days' supply for a home using 600 KWH per month. If one were sure that good weather was on the way, all this stored energy could be used, but usually one would not discharge more than one cell-stack unit (40 KWH) because the charge in the other unit would be needed to start backup generation if the bad weather continued.

In the longer periods of bad weather, the electrochemical engine would be used in the fossil-fueled generation mode to supply 1.1 KW or 25 KWH per day.

We estimate the cost of this electrochemical engine (two cell-stack units) to be well under $1000 with mass production, not including those chemicals which can be recovered. Both lithium and iodine could eventually be transferred into a new engine. Neither is consumed during extended periods of use.

Significant improvements in service could be effected if one hundred electrochemical engines of this design were operated jointly to serve a solar community.

FOCUSING SOLAR COLLECTORS WITH ELECTROCHEMICAL ENGINES

If solar photovoltaics must turn to major focusing and solar tracking, then the possibility of operation in diffuse sunlight is lost. In that case focusing solar energy onto a heat pipe which supplies an electrochemical engine is clearly superior. Here a single device has three functions: solar electric generation, storage, and backup fossil-fueled generation

The 625K used in the preceding calculations could be supplied by tracking Fresnel lenses. Tracking trough collectors such as the Winston collector would also be possible for use with Li/I_2 electrochemical engines.

COMBUSTION OF BIOMASS TO HEAT ELECTROCHEMICAL ENGINES

When Li/I_2 electrochemical engines burn fuel, they are external combustion engines which do not require high-grade heat. In the present design they can operate by burning liquid or gaseous fuels, and even solid fuels can be used if a furnace is attached.

The calculation of electrochemical engine efficiencies with combustion of methane fuel was given two sections earlier in this paper. The generation efficiency with lower-grade fuels often would be slightly lower, e.g., perhaps 25% in converting heat available to electric power. For example, the conversion efficiency with combustion of dry cellulose would be about 26% where methane gave 32%.

SUMMARY

Li/I_2 electrochemical engines look promising for solar-to-electric conversion applications both in connection with photovoltaics and alone with focused solar collection and with combustion of biomass materials.