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**A LIQUID METAL THERMOELECTRIC CONVERTER (LMTEC)
FOR SOLAR APPLICATIONS***

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INTRODUCTION

This presentation consists of an overview of the research and development plan for the Liquid Metal Thermoelectric Converter (LMTEC) being undertaken by Sandia Laboratories under the Solar Thermal Technologies program of DOE. Sandia initiated work in this area less than a year ago and has pursued the work as a specific subtask starting in FY 1985. As with any new project, a significant part of the initial effort has been spent on reviewing the current technology in thermoelectric converters including Thermally Regenerative Electrochemical Systems (TRES), fuel cells, thermionic devices, magnetohydrodynamics, and other modes of direct thermal-to-electric conversion [1,2]. Consequently, no formal research results are included in this paper and the presentation is intended more to indicate those areas in which further research and development efforts could be expended to prove of positive impact on the solar application of LMTEC.

OBJECTIVE

The principal objective of this task is to design, engineer, and develop a LMTEC suitable for use in solar distributed receiver applications. Since the thermal requirements for the LMTEC are in the temperature range of parabolic dishes, the engineering development effort will concentrate on a device that can be mounted at the focal point of a dish and preferably incorporated into the receiver. Due to a technology review, the LMTEC most likely will be based on the current Sodium Heat Engine (SHE) concept invented at the Ford Scientific Laboratory (Ford Motor Company). Our main effort will consist of optimizing the concept for solar applications and conducting the necessary engineering development to produce a 20-50 kW device.

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BACKGROUND AND OUTLOOK FOR A SOLAR LMTEC

The LMTEC is essentially an electrochemical heat engine used for direct thermal-to-electric energy conversion and characterized by the absence of moving mechanical parts. A schematic for such a device depicting the essential components is shown in Figure 1. In such a device a heat source is required to maintain a high temperature, T_H , for the system. A liquid metal, chosen to have a significant vapor pressure, P_H , at T_H is brought in contact with a Beta Alumina Solid Electrolyte (BASE). The BASE material, having the characteristic of being a specific conductor for cations only, is the most critical element of the LMTEC. A pressure differential is induced across the BASE by maintaining a lower temperature, T_L , at which a vapor pressure, P_L , of the metal is significantly reduced. Because of this pressure differential the liquid metal seeks to expand from P_H to P_L . In order to do so, however, it must ionize giving up an electron which by design is forced to travel through an electrical load external to the converter. The molecular or atomic level processes taking place at the interfaces and through the oxygen bridges or metal ion conduction planes of the alumina backbone in the BASE material are depicted in Figure 2. (A more detailed explanation of the principles of operation of a LMTEC is given by Cole [3].) To maintain continuous electron flow the metal ions on the low pressure side of the BASE must be reduced or recombined with electrons. The electrons are brought in by means of a conductive metal electrode of sufficient porosity to allow diffusion of the reduced metal atoms away from the BASE. Once reduced and on the surface of the metal electrode, the metal atoms evaporate and flow to the cooler surface where condensation occurs. The inclusion of a pump (not shown) to return the liquid metal to the high pressure side of the loop completes the thermally regenerative electrochemical system.

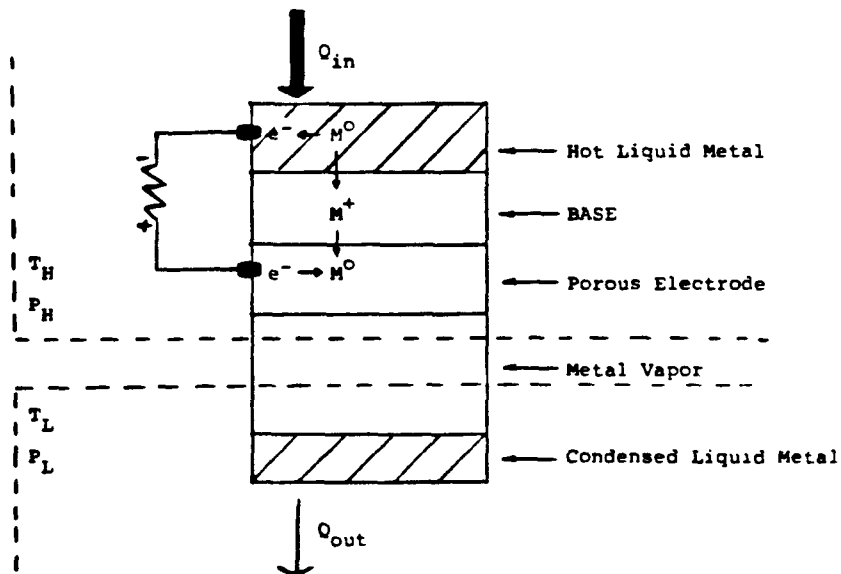


FIGURE 1. LMTEC SCHEMATIC

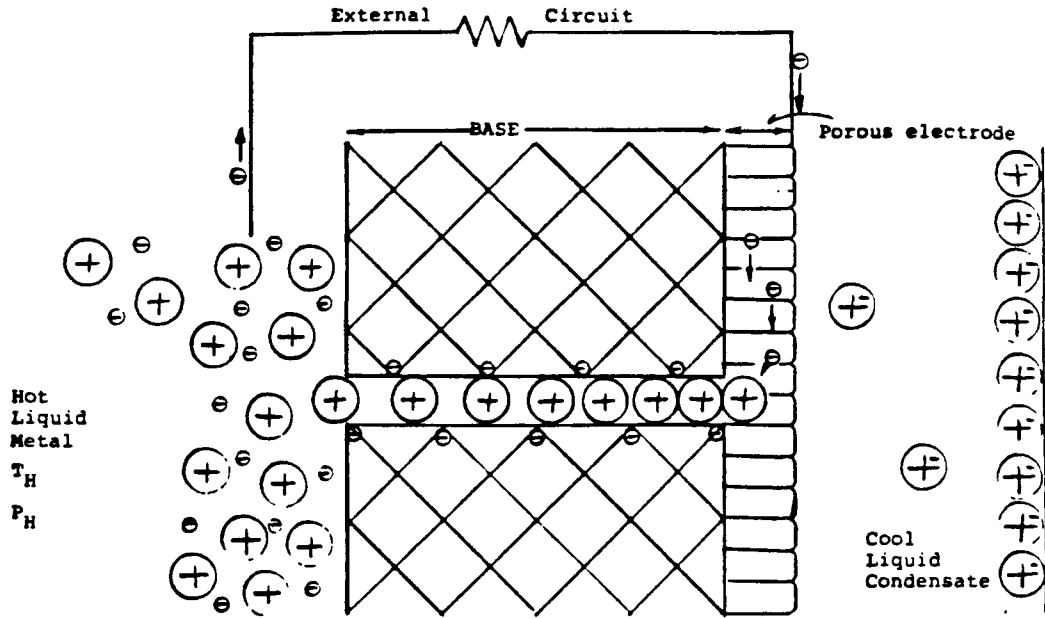


FIGURE 2. ATOMIC LEVEL PROCESSES IN A LMTEC

The Sodium Heat Engine

The SHE, originally developed at Ford and for which a patent was issued in 1968, was the first LMTEC proposed for this purpose. A sketch for such a device depicting very closely the actual demonstration working device is shown in Figure 3. A comprehensive treatment of the thermodynamics and electrochemistry for the SHE was first published by Weber [4]. Expanding the concept to include other alkali metals as working fluids, researches at JPL coined the AMTEC acronym for the Alkali Metal Thermoelectric Converter which has been concisely described by Cole [3].

The potential difference or voltage, E , for the SHE at zero current has been shown to obey the Nernst equation

$$E = \frac{RT_H}{nF} \ln \left(\frac{P_H}{P_L} \right) \quad [1]$$

where: R is the gas constant
 F is the Faraday constant
 n is the number of electrons removed per atom, and
 T_H , P_H , and P_L are as defined previously.

Using the Langmuir assumption that the rate of transport from a surface into a vacuum and the vapor pressure of an evaporating liquid are linearly related, Hunt and co-workers derived a more comprehensive current-voltage relationship for a porous electrode [5]. Their predicted current-voltage plots for different temperatures and a given thickness of BASE parallel very closely their experimentally observed

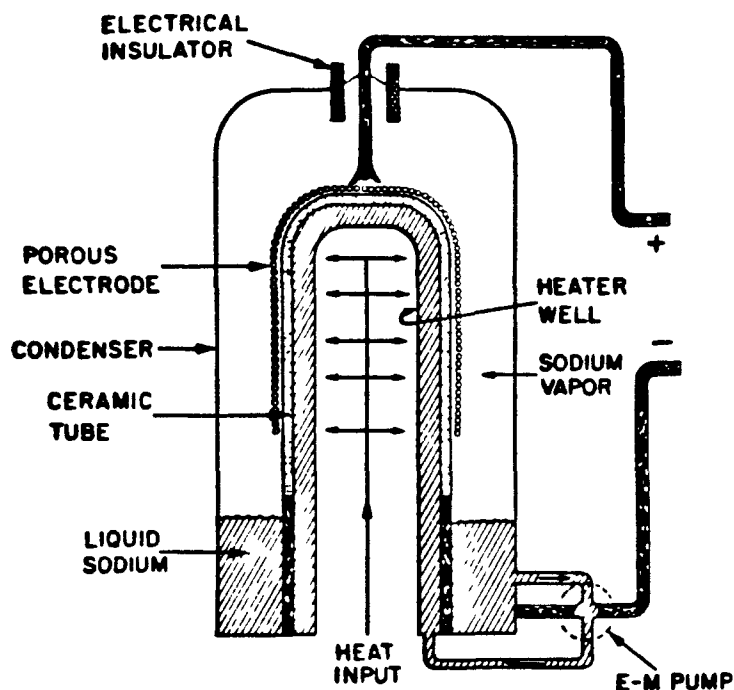


FIGURE 3. SCHEMATIC REPRESENTATION FOR THE SHE

results. While the voltages obtained are very comparable to those achievable with galvanic cells (0.5 to 1 v), the current densities achievable are an order of magnitude higher ($\sim 0.8 \text{ A/cm}^2$). These high current densities have been attributed to the high exchange current density present at the sodium-BASE interface for the SHE.

Power Density

The power-to-weight ratio or power density for a converter is an important parameter. The power density in a LMTEC will be determined primarily by the specific power (Watts/cm^2) of the electrode. For a given T_H and T_L the maximum specific power is inversely proportional to the thickness of the BASE material. Since the BASE material constitutes a key structural element in the SHE design, the effect on its mechanical strength from variations in thickness must also be kept in mind. The SHE devices that have been built have achieved specific powers as high as 1 W/cm^2 using a BASE tube of 0.8 mm thickness. Researchers feel further thinning is possible and that with the incorporation of surface corrugations on the BASE material a specific power of 3 W/cm^2 may be achievable.

The actual power density for a LMTEC will depend on the specific design. Based on the weight of the BASE material alone estimates have been made by Cole [3] at 3.6 kW/kg for the maximum power point with a T_H and T_L at 1200 and 500°K respectively. Since using liquid sodium at these temperatures does not create unduly high pressures (less than 3 atmospheres), thick metal walls should not be required for a larger converter. Estimates have been made that the overall

mass of the converter may not exceed the mass of the BASE material by more than a factor of 5. Power densities of 0.5 to 0.25 kW/kg have been considered in evaluating the advantages of the SHE for solar thermal/electric power conversion by Subramanian and Hunt [6].

Efficiency

The ideal thermodynamic efficiency of the SHE under no load conditions is estimated to be greater than 95% of Carnot [5]. A thermal-to-electric efficiency of 19% was achieved with a SHE that produced 22 watts at 800°C [7]. Using the relation

$$\text{Efficiency} = \frac{W}{W + L + \Delta H + Q_{\text{loss}}} \quad [2]$$

where: W is the electrical work output,
L is the latent heat of vaporization for sodium,
 ΔH is the enthalpy change on heating sodium from T_L to T_H , and
 Q_{loss} includes the radiative heat transfer from the hot positive electrode to the condenser surface, ohmic losses in the electrolyte, and thermal and electrical conduction losses through the output leads,

Hunt and co-workers project that for their concentric cylindrical geometry a thermal-to-electric efficiency of 30 to 40% is possible if the reflectivity of the condenser can be made equal to the reflectivity of molten sodium, and the BASE cross section and output leads are optimized for lead resistance and thermal conduction. Subramanian and Hunt [6] consider an efficiency of 30% achievable in the near term while an advanced design may yield up to 42% efficiency. The authors discuss the improvements to various parameters necessary to achieve such an efficiency.

Electrode Performance

Various electrodes have been tested for the SHE or AMTEC at Ford and JPL. A porous molybdenum electrode applied by either chemical vapor deposition or magnetron sputtering has achieved 90% of the theoretical voltage output predicted [7]. The electrodes, however, show a gradual drop in specific power output with time at high temperature. After extended hours of operation (>200 hours) the performance of the electrodes decays asymptotically to 1/2 to 1/5 of the initial specific power [3,7]. Recent reports from T. K. Hunt indicate that a long-term stable electrode has been achieved with a specific density of 0.3 W/cm².

Summary of Salient Characteristics for LMTECs

Based on the foregoing paragraphs, several positive characteristics of the SHE and presumably applicable to LMTEC are evident.

- An isothermal expansion process is thermodynamically advantageous because of the higher extractable theoretical work as opposed to an adiabatic expansion process.
- The absence of moving parts alleviates the concerns over mechanical wear with extended use and is conducive to low parasitic power requirements.
- The demonstrated 0.3 W/cm^2 specific power density is suitable for engineering development of a solar LMTEC. The near and far term achievable specific power densities of 0.5 and 1.0 W/cm^2 can only improve the outlook.
- The projected efficiency of the LMTEC is on a par with conventional heat engines. Furthermore, the efficiency appears to be independent of size and should allow for adaptation of LMTECs for various dish sizes.
- The parasitic requirements for circulating the liquid metal should be low ($<1\%$).
- The rejected heat at T_L (ca. 300°C) is of sufficient quality to allow for incorporation of existing or potential bottoming cycles.
- Since multiple heat sources can be used for LMTEC, the flexibility exists for considering the various hybrid modes of operation proposed for solar installations.

ENGINEERING DEVELOPMENT PLAN FOR LMTEC

The planned approach for the engineering development of a LMTEC as indicated in our two-year plan for FY 1985 and 1986 can be broken down into the following areas:

- Review the solid electrolyte heat engine technology.
- Design, fabricate, and test a LMTEC based on sodium.
- Investigate alternatives to the use of sodium as a working fluid in order to allow operation at optimum efficiency and possibly lower temperatures.
- Compare the use of LMTEC technology to the use of conventional heat engines and other possible electric conversion techniques such as MHD.

- Address the various solar application engineering development issues.

The first area has been essentially completed and the technology review concluded that competing thermoelectric conversion systems are characterized by one or more of the following three drawbacks:

- Low efficiencies,
- High temperature requirements, and/or
- Low power densities

Our findings concur with those of Chum and Osteryoung [2] and point to the SHE as the most promising of the TRES devices based on the extensive research which has thoroughly addressed the theory. It is the feeling of those currently working on this technology that the concept is mature enough for engineering development.

Some key problem areas alluded to by researchers currently working on this technology and which must be seriously addressed in the engineering development include:

- The mechanical properties of the ceramic BASE material, namely the low thermal shock resistance as well as the need for matching the coefficient of thermal expansion with different materials.
- The decay in performance of the porous molybdenum electrode.
- The techniques used for collecting the electric current require sizable electric conductors which can lead to significant conductive losses on interconnecting multiple operating cells.
- The priming of the EM pump has been a problem on start-up for the SHE because of the difficulty of getting sodium to enter a small tube.
- The vacuum requirements demand that a near hermetic seal be effected between a ceramic and a metal.
- Other thermal, flow, and resistive loss mechanisms that can detract from the efficiency of the system.

Analyzing these problems in the context of a solar application, one can anticipate the engineering design measures that will have to be undertaken in the development of LMTEC.

- The problems with the BASE material could possibly be intensified on a dish mounted device due to changing orientations which could cause the condensed, cold liquid metal to fall on the hot BASE material and crack it due to the low thermal shock resistance. Diurnal thermal cycling inherent in a solar application

as well as thermal gradients associated with solar receivers must also be considered in the engineering design.

- The porous electrode performance as presently developed does not constitute a severe problem as such to a solar design. One possible impact is on the volume of the LMTEC even if it is light in weight.
- The techniques for collecting the electric current affect the schemes one can use for interconnecting the individual cells.
- The priming of the EM pump may present a problem for solar applications with daily start-ups. The location of a pump in a receiver with changing orientations will also be critical.
- The requirement for a pressure difference presents a problem due to the multiple seals required between the BASE and a metal.
- The various loss mechanisms will require optimization of various parameters so as to get the maximum possible efficiency.

Other anticipated problems involve receiver issues such as the best method of coupling to a LMTEC and achieving optimum heat transfer. With the currently achieved electrode performance, the issue of incorporating the necessary surface area of BASE in a receiver ($\sim 5 \text{ m}^2$ for 25 kWe using a 0.3 W/cm^2) while allowing for adequate heat transfer may not be trivial. The modularity of LMTECs will require multiple interconnections at a high temperature in order to minimize conductive thermal losses. At the same time conductor sizes and lengths will require optimization in order to minimize I^2R losses.

The expected solar performance of a LMTEC places a high priority on maximizing the efficiency since the system must compete with existing and potential conventional heat engines. An effort must also be made to keep the capital costs down so as not to overshadow the significant advantage anticipated for a LMTEC in O&M costs.

Since our intent is to concentrate on the engineering development of LMTEC, our approach to date has been to:

- Undertake a conceptual design of a solar LMTEC.
- Design and construct a LMTEC to serve as an engineering test bed to help evaluate solar specific design concepts, to provide experimental verification for analytical models, and to support materials investigations.
- Stress problem areas not currently under investigation; specifically, sponsor work on an exchanged BASE material for alternate working fluids.
- Promote the engineering development work necessary to design and fabricate a 20-50 kWe LMTEC that can operate at the focal point of a parabolic dish.

PROGRESS MADE TO DATE

To date our progress can be summarized in three major areas:

- We have performed systems analyses that indicate LMTEC is a viable option for dish electric.
- We have initiated conceptual design studies of LMTEC for dish electric, including thermodynamic modeling of the LMTEC operating parameters as well as heat transfer and structural modeling. The design studies have suggested several proof-of-concept experiments which must be demonstrated before a final design can be put together. One such demonstration includes the formation of a continuous film of liquid metal on BASE material in the presence of metal vapor. An equally important experiment is one to demonstrate a liquid metal-free insulating surface in the presence of high temperature metal vapor. For a bipolar design similar to that of fuel cells it is important to demonstrate that an effective seal suitable for a hot liquid metal can be accomplished on stacked plates.
- Work sponsored in the search for an alternate working fluid has resulted in the exchange of other metal ions for sodium ions in single crystals of BASE material. Work is continuing in this area to measure the conductivity of the mercury exchanged material as well as to conduct the exchange in polycrystalline material and measure the mechanical stability and conductivity at various operating temperatures.

CONCLUSION

Based on our review of the technology and the work performed to date, the LMTEC has great potential for use in dish-electric applications and the plan is to continue its engineering development because of its inherent advantages. Preliminary economic analyses based on the dish electric system studies appear enticing. The concensus is that the current technology is ripe for engineering development. The fact that the technology lends itself to further optimization is a strong recommendation to pursue it.

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REFERENCES

1. Angrist, S. W., Direct Energy Conversion, Fourth Edition, Allyn and Bacon, Inc., Boston, 1982.
2. Chum, H. L., and Osteryound, R. A., "Review of Thermally Regenerative Electrochemical Systems," SERI Report TR-332-416, 1981.
3. Cole, T., "Thermoelectric Energy Conversion with Solid Electrolytes," Science, 221, (1983), p. 915.
4. Weber, N., "A Thermoelectric Device Based on Beta-Alumina Solid Electrolyte," Energy Conversion, 14, 1, (1974), p. 1.
5. Hunt, T. K., and Cole, T., "Research on the Sodium Heat Engine," Proc. Inter-Soc. Energy Conv. Engr. Conf., (1978), p. 2011.
6. Subramanian, K., and Hunt, T. K., "Solar Thermal/Electric Power Conversion Using the Sodium Heat Engine," Proc. 5th Annual Conf. of ASME Solar Energy Div. (1983), p. 288.
7. Hunt, T. K., Weber, N., and Cole, T., "High Efficiency Thermoelectric Conversion with Beta"-Alumina Electrolytes, the Sodium Heat Engine," Proc. of Intern. Conf. on Fast Ion Transport in Solids, (1983), p. 277.