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Review of Thermally Regenerative Electrochemical Systems

Volume 1: Synopsis and Executive Summary

Helena L. Chum
Robert A. Osteryoung

Solar Energy Research Institute
A Division of Midwest Research Institute

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Golden, Colorado 80401

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REVIEW OF THERMALLY REGENERATIVE ELECTROCHEMICAL SYSTEMS

VOLUME 1: SYNOPSIS AND EXECUTIVE SUMMARY

HELENA L. CHUM
ROBERT A. OSTERYOUNG

AUGUST 1980

PREPARED UNDER TASK NO. 3356.10

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PREFACE

This review was prepared by R. A. Osteryoung, formerly with Colorado State University and now with the State University of New York at Buffalo, and by H. L. Chum, formerly with Colorado State University and presently on the SERI staff. Work was performed largely under Contract No. AM-9-8078-1 and SERI Task 3356.10. Compiled in two volumes, the review covers the technical background of thermally regenerative electrochemical systems and presents recommendations for further work. For the reader interested in a general overview, Volume 1, Synopsis and Executive Summary, is a condensed version of Volume 2. Volume 2, which discusses the thermally regenerative electrochemical systems in more detail, is intended for researchers in chemical and electrochemical areas and for engineers (although detailed coverage of the fields of engineering, corrosion, and materials problems is outside the scope of this report).

The authors wish to acknowledge T. A. Milne for the suggestion of the subject of this report and for helpful discussions. During the course of this review, discussion took place with a number of people involved in research and development of fuel cells and/or regenerative electrochemical systems. Among these were J. Appleby, B. Baker, M. Breiter, E. Cairns, T. Cole, G. Elliot, E. Findl, A. Fischer, F. Gibbard, L. Heredy, J. Huff, T. Hunt, C. Johnson, R. Kerr, M. Klein, K. Kordesch, F. Ludwig, J. McBreen, L. Nanis, W. O'Grady, J. Plambeck, H. Shimotake, H. Silverman, R. Snow, S. Srinivasan, C. Tobias, R. Weaver, N. Weber, and E. Yeager. These discussions were very helpful. Special thanks are due to J. H. Christie for profitable discussions and careful editing of the manuscript. The technical support of the Colorado State University Library and the Solar Energy Information Center is gratefully appreciated.

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SYNOPSIS

OBJECTIVE

Thermally regenerative electrochemical systems (TRES) are closed systems that convert heat into electricity in an electrochemical heat engine that is Carnot cycle limited in efficiency.

In this report, past and present work on TRES is reviewed and classified. Two broad classes of TRES can be identified according to the type of energy input required to regenerate the electrochemical cell reactants: thermal input alone (Section I and II) or the coupling of thermal and electrolytic energy inputs (Sections III-V). To facilitate the discussion, these two broad categories are further divided into seven types of TRES (Types 1-3 for thermal regeneration; Types 4-7 for coupled thermal and electrolytic regeneration). The subdivision was made according to significant differences in either the electrochemical cells or in the regenerators.

DISCUSSION

In Type 1 TRES, compound CA is formed from C and A in an electrochemical cell at temperature T_1 with concomitant production of electrical work in the external load. Compound CA is sent to a regenerator unit at T_2 through a heat exchanger. In the regenerator, compound CA is decomposed into C and A, which are separated and redirected to the electrochemical cell via a heat exchanger, thus closing the cycle. The thermodynamic requirements for the electrochemical reaction are $\Delta G < 0$, $\Delta S < 0$, and ΔC_p as close to zero as possible. This type of TRES is equivalent to a primary battery, in which electrodes A and C are consumed. By coupling the battery with a regenerator unit, the electrode materials are regenerated. The classes of compounds that were investigated or proposed for this type are metal hydrides, halides, oxides, and chalcogenides. One of the most thoroughly investigated systems is the lithium hydride system (T_1~500°C, T_2~900°C). The advantage of this system is that lithium hydride decomposes into liquid lithium and gaseous hydrogen, enabling relatively simple separation. The power delivered by this system was low. Problems were encountered in the gas electrode, in the rate of decomposition of lithium hydride, and in materials. The best conditions for the electrochemical cell and for the regenerator were never realized in a practical system. A considerable fraction of the compounds investigated or proposed had T_2~800°-900°C. Nuclear reactors were the heat source envisioned for that temperature range. Some materials decomposing at lower temperatures were tried. An example is antimony pentachloride, which decomposes at ~300°C into liquid antimony trichloride and gaseous chlorine; however, the performance of the electrochemical cell was very poor. All of the above systems had one electrochemical reaction product and the regeneration was accomplished in a one-step process. An interesting example of a system in which two electrochemical reaction products are regenerated in one step has long been known. It involves the oxidation of tin and the reduction of chromium (III) species at a graphite electrode in the electrochemical cell generating power. The regeneration is accomplished by lowering the temperature when the spontaneous reverse reaction takes place. This is a periodic power source.

Type 2 is similar to Type 1, but the products C and E of the electrochemical cell reaction A + D → C + E are regenerated in a two-step process (C → A + B; E + B → D). It involves more complex plumbing and two regenerator units. The systems attempted include metal halides or oxides; for example, A = tin (II) or tellurium (II) chloride and D = antimony (V) or copper (II) chloride with B = gaseous chlorine. If at the regeneration temperatures A is also in the gaseous state, the separation of A and B is the major obstacle to successful operation of this type of system. To date, no complete electrochemical cell coupled with the regenerator has been demonstrated to be feasible.

Type 3 is also similar to Type 1 and involves a one-step regeneration. Liquid metal electrodes are composed of one electroactive metal C and one electroinactive metal B. C and B form alloys C(B) or bimetallic compounds C_xB_y. The anode and the cathode have, respectively, high and low concentrations of the electroactive metal in the liquid electrode. The cells are concentration cells. The regeneration is accomplished by sending the electrode materials (combined or individually) to a distillation unit where the C+B mixture is separated into C-rich and C-poor components, which are returned to the anode and cathode compartments, respectively. Examples include C = sodium or potassium and B = mercury or lead. These are the systems for which the feasibility of the thermal regeneration coupled to the battery was demonstrated. The performance of the demonstrated systems was poor, due in part to constraints imposed by the space applications envisioned. The performance of this type of system can be improved.

In Type 4 systems, compound CA, formed in the electrochemical cell at temperature T_1, is sent to a regenerator, which is an electrolysis cell at temperature T_2. In the regenerator, reactions opposite to those occurring at T_1 regenerate C and A by using two energy inputs--electric and thermal. The electrolysis cell uses a fraction of the voltage produced by the battery at T_1 (the additional energy is supplied as heat) and the remaining voltage is used to perform work in the external load. These systems are analogous to, and have the same requirements as, secondary (rechargeable) batteries. A few systems have been investigated; for example, CA = sodium chloride, lead iodide, cadmium iodide, lithium iodide. If C and A are in the gaseous state (for instance, hydrogen and oxygen), the electrochemical cell is a fuel cell; the regeneration is performed by water electrolysis at high temperature. To date, no complete demonstration of the feasibility of these systems has been performed. In addition to the above-mentioned examples of high temperature electrolysis, very few systems operating at lower temperature were explored in this mode of regeneration.

Type 5 systems are a particular case of Type 4, in which the electrolysis is performed at low pressure. They include systems in which one of the electroactive species is in the gaseous state. The battery and the electrolysis cell operate at the same temperature, and the pressure of the electroactive species is varied in these two cells by physical means, e.g., by the coupling of the cells with cold fingers. The operation is periodic. Examples include gaseous iodine as the working electroactive fluid in lithium|molten iodide|iodine cells. Low voltages are expected from these devices as well as mass transfer problems. However, these systems have energy storage capability.

In Type 6 systems, or thermogalvanic or nonisothermal cells, the two electrodes are at different temperatures and the cell temperature is not uniform. The electrodes can be metallic, liquid, or gaseous (with inert electrodes). The electrolyte can be solid or liquid, homogeneous or heterogeneous. During the passage of current through the thermogalvanic cell, matter is transferred from one electrode to the other as a result of the electrochemical reactions at the electrode/electrolyte interface and ionic transport in the electrolyte. In some types of cells the transfer of matter is permanent, and therefore a mechanical means to reverse the temperature of the electrodes must be provided for continuous operation of the engine as a power source. In these cells the thermal and electrolytic paths are not separated. Examples include copper electrodes immersed in a variety of copper salt solutions and gaseous chlorine in solid electrolyte or molten salt media. Most data for these cells refer to scientific information (e.g., irreversible thermodynamics) and not to power generation. The systems generate low power outputs but can be made much more cheaply than their solid-state analogs.

Type 7 engines are based on pressure differences of the working electroactive fluid across an isothermal electrolyte (solid or liquid). The pressure difference is maintained by using the changes in the vapor pressure with the temperature of the working electroactive fluid. The work performed is equivalent to the isothermal expansion of the working electroactive fluid from the high to the low pressure zone at T_2 through the electrolyte and its interfaces. After expansion, the working fluid is condensed in a cold reservoir and can be recycled to the high temperature, high pressure zone of the cell by means of a pump. The cells are concentration cells. Because the working fluid does not undergo chemical changes, no regeneration and separation steps are necessary. Examples include iodine vapor expanded through isothermal liquid lead iodide and sodium vapor expanded through isothermal solid beta-alumina electrolyte. In the first example, the major difficulty is maintainance of the liquid electrolyte integrity when it is subjected to a pressure gradient. In the second example (T_1~200°-300°C, T_2~800°-900°C), this problem is avoided by using a solid superionic conductor electrolyte. The highest power outputs in TRES to date have been obtained with this type of engine. The present nonavailability of other superionic conductors limits the extension of this concept to other practical energy converters.

CONCLUSIONS AND RECOMMENDATIONS

TRES cover temperature ranges from near room temperature to about 1200°C. To date, power outputs of 0.1 mW/cm^2 to about 1 W/cm^2 have been achieved. The majority of the systems reported utilized molten salt electrolytes and high regeneration temperatures. In addition, several promising energy converters employed solid electrolytes, which are superionic conductors. Much less explored are lower-temperature media--aqueous, nonaqueous, or molten salt. Little effort was expended on the use of catalysts to improve the rates of thermal decomposition. General problems included engineering and materials problems. A considerable fraction of the research and development of these engines was performed around 15 to 20 years ago in connection with the production of secondary space power sources to utilize heat from nuclear reactors.

In this report we recommend areas of research in either science or engineering that would have long-range benefit to a TRES program. These areas include molten salt chemistry and electrochemistry, solid-state chemistry, materials sciences, aqueous systems and electrochemistry under extreme conditions, electrochemical engineering, and systems analysis. It should be pointed out that because solar-derived heat covers a very wide range of temperatures (~80°-1000°C), more TRES can be brought into consideration.

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EXECUTIVE SUMMARY

INTRODUCTION

OBJECTIVE

This review of thermally regenerative electrochemical systems (TRES) was written upon request of T. A. Milne of the Chemical and Biological Division of the Solar Energy Research Institute. The bulk of the information contained in this report was collected from February to October 1979. The information comes from literature searches and from visits to the laboratories of, and discussions with, technical personnel involved with this type of research. Work on TRES has been classified and analyzed, with emphasis on the operation of the electrochemical systems. It is important to emphasize, however, that TRES involve the merging of several disciplines in addition to electrochemistry: thermal conversion, engineering, materials science, etc. The purpose of this review is to aid evaluations of the electrochemical technique of direct thermal-to-electrical conversion.

The majority of the systems published in the open literature or patented are reviewed. Because this area was developed from the late fifties to the late sixties with the utilization of heat from nuclear reactors as a major mission, most of the systems operated at high temperatures. Our review covers these systems and a variety of others developed or proposed, which operate under a wide variety of conditions. A cross-comparison, or ranking, of systems for different missions, at different stages of development, and at different operating conditions is not feasible for this review.

The systems investigated in the past are reviewed in detail in Vol. 2 and more briefly in the Executive Summary. It is our purpose to suggest areas of research (in either science or engineering) that would benefit from a long-range TRES program, rather than to propose specific systems for further device exploration. In the past, most of the funding and expectations were device oriented in short-term programs. The systems for which there existed a better understanding of the chemical, electrochemical, engineering, and materials problems were pursued in relatively long-term and research-oriented projects.

The Executive Summary has the same structure as Vol. 2, so that references and further technical background can be located easily.

BACKGROUND

Regenerative electrochemical systems were one of a variety of complex methods of energy conversion investigated during the period from 1958 to 1968. In these systems the working substance produced in an electrochemical cell (fuel cell, battery, galvanic system, emf cell) is regenerated by the appropriate input of energy (thermal, light, atomic, electrical, or chemical), thereby defining the thermal, photo-, nuclear, electrolytic, or redox regenerative electrochemical systems [1]. The major heat source envisioned during this period was nuclear reactor heat. Direct use of sunlight for photoregeneration also was attempted, as well as use of nuclear radiation. The electrolytically regenerative systems are essentially indistinguishable from secondary batteries and were explored chiefly for their possible utilization in load leveling, for their storage capability, and for space-flight application. The redox systems appeared particularly attractive because of their energy storage capability [2].

Austin [3] critically reviewed the government-sponsored fuel cell research from 1950 to 1964, including regenerative types, for possible space power application or for silent and portable electric generators. Kerr [4] reviewed work up to 1967, comparing the different types of regeneration for space power application. Nuclear, photo-, and redox systems were eliminated from consideration due to weight, complexity, and low efficiency. The proceedings of a symposium on regenerative emf cells [5], published in 1967, includes discussion of most types of regenerative systems.

Because of the low overall efficiencies [3,4,5] of the regenerative systems due to Carnot cycle limitations (thermal), problems of pumping, plumbing and separation (thermal and nuclear), and low quantum yields (photo-), research after 1968 was concerned primarily with electrolytic regenerative [6] and redox [2] systems. However, because thermal energy can be obtained by harnessing the sun's rays, it is possible to envision TRES operating under conditions that differ markedly from those offered by nuclear reactors. It is therefore conceivable, as pointed out by Kerr [4], that the problems of TRES for some applications are surmountable. In this report, we classify thermally regenerative electrochemical systems as systems regenerated by the input of thermal or coupled thermal and electrolytic energy. Because the seven types of TRES have unique features, a general introduction is not given at this point.

TYPES OF THERMALLY REGENERATIVE ELECTROCHEMICAL SYSTEMS

Thermally regenerative electrochemical systems are closed systems that convert heat into electricity in an electrochemical heat engine that is Carnot-cycle limited in efficiency. In this report the TRES have been classified into two broad classes: systems regenerated thermally and systems regenerated by a coupling of thermal and electrolytic inputs. To facilitate discussion, the types of TRES within these two broad classes have been designated according to significant differences in either the electrochemical cells or regenerators.

Sections I and II concern thermal regeneration, and the following three types of TRES are defined:

Type 1.

Figure S-1 illustrates this type of system. The electrochemical reaction product CA is formed from C and A in an electrochemical cell at T_1, with concomitant production of electrical work in the external load. For such a production of electricity to be continuous, compound CA must be easily decomposed into C and A. Thus, compound CA is sent to a regenerator at T_2 via a heat exchanger. In the regenerator, the thermal decomposition reaction takes place spontaneously. Compounds C and A formed in the regenerator at T_2 are separated by physical (or chemical) means, and the isolated compounds C and A are returned to the electrochemical cell after being returned to temperature T_1 through the heat exchanger, thus completing the cycle. The most favorable thermodynamic properties of the electrochemical reaction for a thermally regenerative electrochemical system are: $\Delta G < 0$, $\Delta S < 0$, and ΔC_p as close to zero as possible.

Type 2.

Figure S-2 illustrates this type of system. In this case, a more complex set of galvanic cell reactions occurs at T_1. Two or more products are formed in the electrochemical reaction; therefore, the regeneration of the anode and cathode materials (A and D) must be performed separately at T_2 and T_3, as indicated in Fig. S-2. It is a more complex scheme, requiring more plumbing, heat exchangers, and regenerator chambers than the simple system of Type 1.

Type 3.

Figure S-3 illustrates this type of system. In principle, this scheme is identical to that of Type 1. However, it applies to specific cases in which the electrochemical cell reaction involves only one electroactive couple C^+/C in a concentration cell at T_1. C(B) represents, for instance, an alloy or a bimetallic compound.

Sections III, IV, and V concern coupled thermal and electrolytic regeneration, and the following four types of TRES are defined:

Type 4.

As illustrated in Fig. S-4, compound CA formed in the galvanic cell at T_1 is sent to a regenerator at T_2 via a heat exchanger, where it is electrolytically decomposed into C and A. The requirements for this type of regeneration are that the cell reactions $C \rightleftarrows C^+ + e^-$ and $A + e^- \rightleftarrows A^-$ are reversible and of high coulombic efficiency and high exchange current. In addition, the voltage $V(T_1)$ must be larger than $V(T_2)$. The cells are connected in electrical opposition and the electrolysis takes place consuming $V(T_2)$. The remaining voltage can be used to perform useful work in the external load. The separation is inherent in this type of regeneration. Compounds C and A are returned to the galvanic cell via heat exchangers, and the loop is closed. If at a temperature T_x the reverse reactions of reactions in the galvanic cell take place spontaneously, then the regeneration produces an additive voltage $V(T_x)$ while regenerating C and A at T_x.

Type 5.

This type is illustrated in Fig. S-5. Two galvanic cells at the same temperature are arranged so that the activity of one of the electroactive species can be varied by some physical means. In the example shown, a cold finger reduces the pressure of the gaseous working electroactive fluid A. The galvanic cells are connected back to back. The galvanic cells are concentration cells in the A/A^- species. As cell 1 discharges, cell 2 charges and work is performed in the external load proportional to the differences in activities of A in the two cells. The operation is interrupted as A-rich material is consumed. The switch reaction corresponds to heating the cold finger associated with cell 2 and cooling that associated with cell 1. The roles of the two cells are now reversed and the system can again perform electrical work in the external load. This scheme is equivalent to an electrolysis performed at reduced pressure. Mass transfer could be the major limitation to this type of TRES.

Type 6.

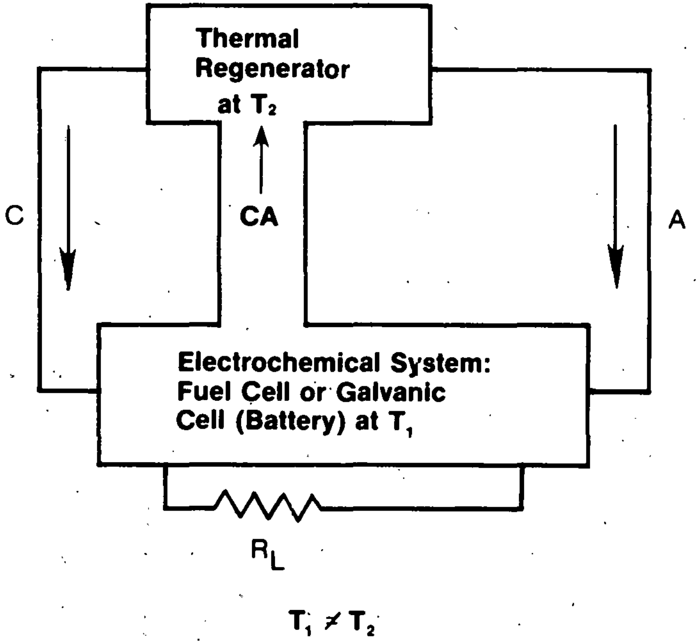
This type of TRES is illustrated in Fig. S-6. The thermal and electrolytic paths are not separated. Two or more electrodes are at different temperatures. These electrodes (not necessarily chemically identical or reversible) are in contact with the electrolyte (liquid or solid, not necessarily homogeneous in composition, and with or without permeable membranes interposed in the electrolyte), in which a temperature gradient exists. These TRES are called thermogalvanic or nonisothermal cells. During the passage of current in the cells, matter is transferred from one electrode to the other as a result of the electrochemical reactions at the electrolyte/electrode interfaces and ionic conduction.

If the transfer of matter is permanent, as occurs with electroactive metal electrodes, the electrodes must have their temperatures reversed periodically for continuous operation of the engine as a power source. This temperature reversal operation can be avoided if gas electrodes, or redox soluble couples, are used. These thermogalvanic cells are the electrochemical analogs of thermoelectric devices. The efficiency in these devices is related to the Carnot efficiency. The upper limit is determined by the use of expressions developed for solid-state, thermoelectric devices. These equations take into account the Carnot efficiency, the thermal and electrical conductivities, and the thermoelectric power (dE/dT) of the system, but they do not take into account electrode polarization effects characteristic of the electrochemical reactions.

Type 7.

In this type, illustrated in Fig. S-7, the thermal and electrolytic paths are separated. An isothermal electrolyte (solid or liquid) separates the working electroactive fluid from two pressure regions. The work performed in these engines is equivalent to the isothermal expansion of the fluid from the high pressure, high temperature zone (P_H,T_H) to a low pressure zone (P_L,T_H) separated by the electrolyte and created by cooling one end of the engine. The element C undergoes oxidation, the electrons traverse the external circuit, and ions C^+ cross the electrolyte as a result of the pressure differential across the electrolyte. The C^+ ions are reduced at the electrode attached to the bottom of the electrolyte, at a lower pressure. At the cold trap, C is condensed. To produce electricity continuously with these engines, C(P_L,T_L) must be pumped to C(P_H,T_H). These engines do not need a chemical separation step.

Table S-1 presents a summary of typical examples of all seven types of TRES. Inspection of the table shows that these systems can cover various ranges of temperatures from near room temperature to 1000°C. In the systems studied to date, powers of 0.1 mW/cm^2 to 1 W/cm^2 have been achieved. Emphasis in past work was placed on systems regenerated at high temperatures.



Electrochemical Cell Reactions

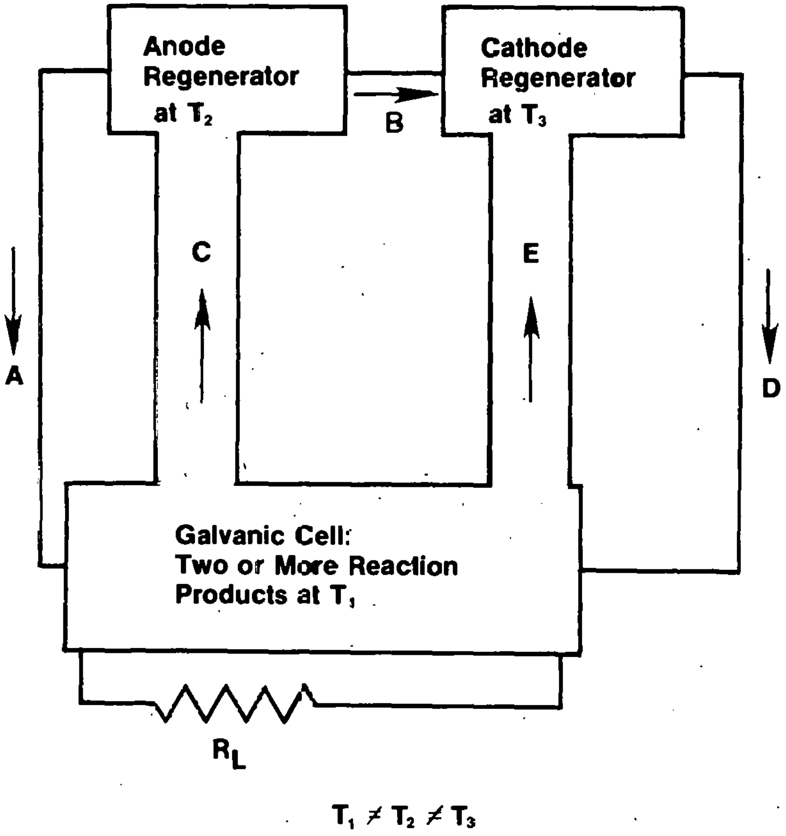
$$\left\{\begin{array}{lll} C \longrightarrow C^{+} + e^{-} & \text{Anode} \\ A + e^{-} \longrightarrow A^{-} & \text{Cathode} \\ \hline C + A \xrightarrow{T_1} CA & \end{array}\right.$$

Heat Exchange $CA(T_1) \longrightarrow CA(T_2)$

Thermal Regenerator $CA \xrightarrow{T_2} C + A$

Heat Exchange $C + A\ (T_2) \longrightarrow C + A\ (T_1)$

Figure S-1. Thermal Regeneration: Type 1



Galvanic Cell Reactions

$$\left\{\begin{array}{ll} A + B^- \longrightarrow C + e^- & \text{Anode} \\ D + e^- \longrightarrow E + B^- & \text{Cathode} \\ \hline A + D \xrightarrow{T_1} C + E & \end{array}\right.$$

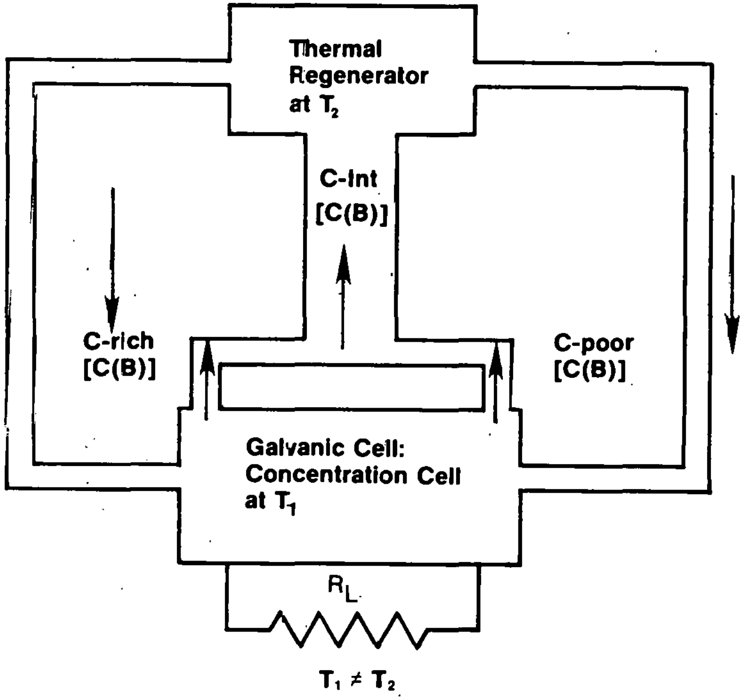
Heat Exchange $C(T_1) \longrightarrow C(T_2)$; $E(T_1) \longrightarrow E(T_3)$

Anode Regeneration $C \xrightarrow{T_2} A + B$

Cathode Regeneration $E + B \xrightarrow{T_3} D$

Heat Exchange $A(T_2) \longrightarrow A(T_1)$; $D(T_3) \longrightarrow D(T_1)$

Figure S-2. Thermal Regeneration: Type 2



Electrochemical Cell Reactions

$$\left\{\begin{array}{ll} \text{C-rich [C(B)]} \longrightarrow \text{C}^+ + e^- & \text{Anode} \\ \text{C}^+ + e^- \longrightarrow \text{C-poor [C(B)]} & \text{Cathode} \\ \hline \text{C-rich [C(B)]} \xrightarrow{T_1} \text{C-poor [C(B)]} & \end{array}\right.$$

Heat Exchange

$$\text{(C-rich + C-poor)[C(B)]}_T \longrightarrow \text{C-Int [C(B)]}_{T_2}$$

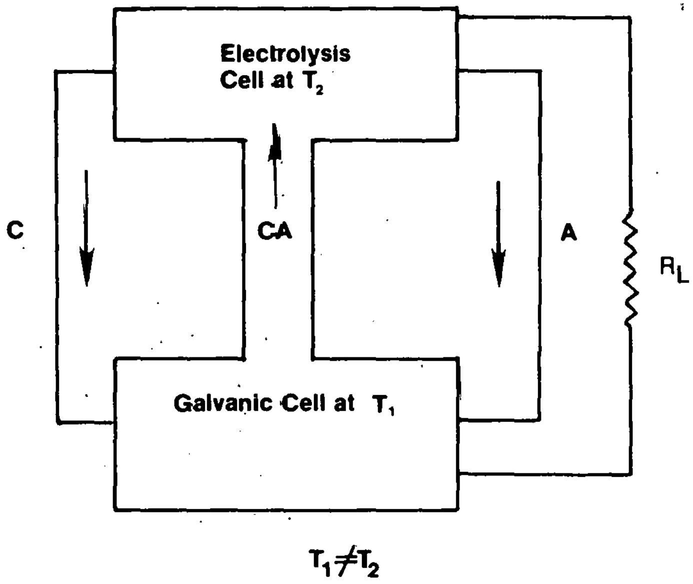
Thermal Regenerator

$$\text{C-Int [C(B)]} \xrightarrow{T_2} \text{C-poor [C(B)] + C-rich [C(B)]},$$

Heat Exchange

$$\text{C-poor [C(B)]}T_2 + \text{C-rich [C(B)]}_{T_2} \longrightarrow \text{C-poor [C(B)]}_{T_1} + \text{C-rich [C(B)]}_{T_1}$$

Figure S-3. Thermal Regeneration: Type 3



Galvanic Cell Reactions

$$\left\{\begin{array}{lll} C \longrightarrow C^+ + e^- & & \text{Anode} \\ A + e^- \longrightarrow A^- & & \text{Cathode} \\ \hline C + A \xrightarrow{T_1} CA & & \end{array}\right.$$

Heat Exchange

$$CA(T_1) \longrightarrow CA(T_2)$$

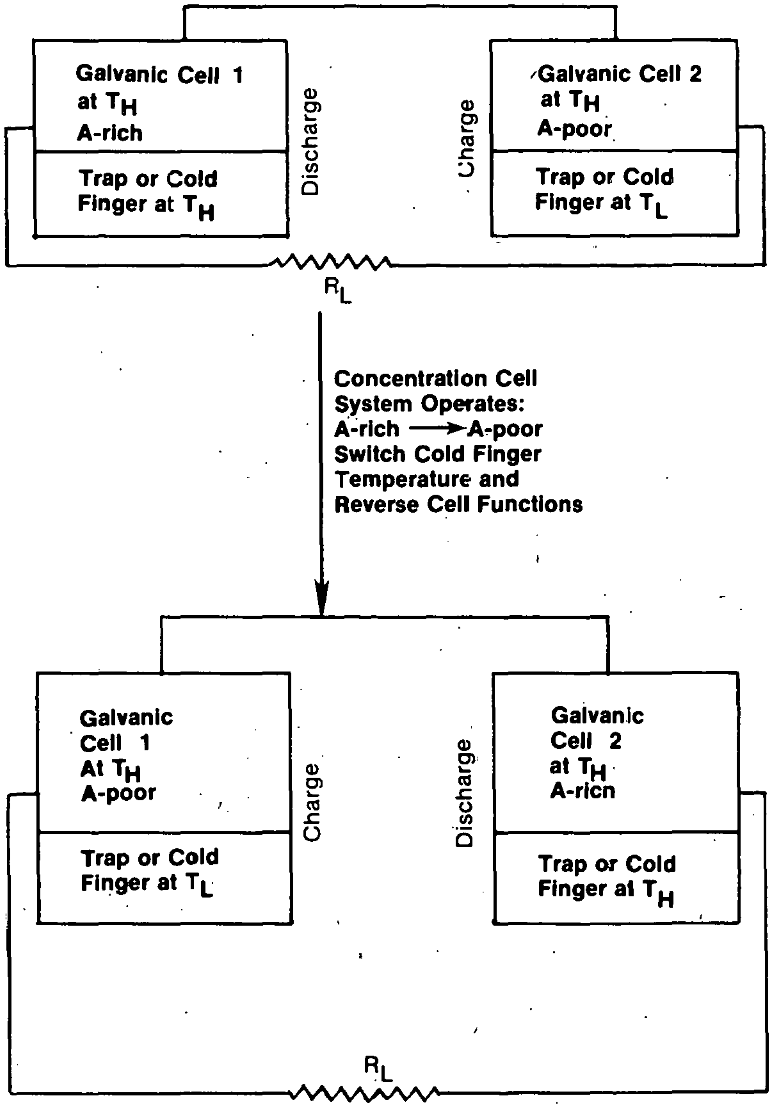
Electrolysis Cell Reactions

$$\left\{\begin{array}{lll} A^- \longrightarrow A + e^- & & \text{Anode} \\ C^+ + e^- \longrightarrow C & & \text{Cathode} \\ \hline CA \xrightarrow{T_2} C + A & & \end{array}\right.$$

Heat Exchange

$$[C + A](T_2) \longrightarrow [C + A](T_1)$$

Figure S-4. Coupled Thermal and Electrolytic Regeneration: Type 4



Electrolysis at Low Pressure

Electrochemical Cell 1 Reactions (Discharge)

$C \longrightarrow C^+ + e^-$ Anode

$A\text{-rich} + e^- \longrightarrow A^-$ Cathode

$C + A\text{-rich}(g) \xrightarrow{T_H} CA$

Electrochemical Cell (2) Reactions (Charge)

$A^- \longrightarrow A(g) + e^-$ Anode

$C^+ + e^- \longrightarrow C$ Cathode

$CA \xrightarrow{T_H} C + A(g)$

Cold Finger

$A(g)_{T_H} \rightleftharpoons A(l\ \text{or}\ s)_{T_L}$

Switch Reaction (No Power to External Circuit)

Cell 1 Cold Finger at T_L

Cell 2 Cold Finger at T_H

Electrochemical Cell 1 Reactions (Charge)

$A^- \longrightarrow A(g) + e^-$ Anode

$C^+ + e^- \longrightarrow C$ Cathode

$CA \xrightarrow{T_H} A(g) + C$

Cold Finger

$A(g)_{T_H} \rightleftharpoons A(l\ \text{or}\ s)_{T_L}$

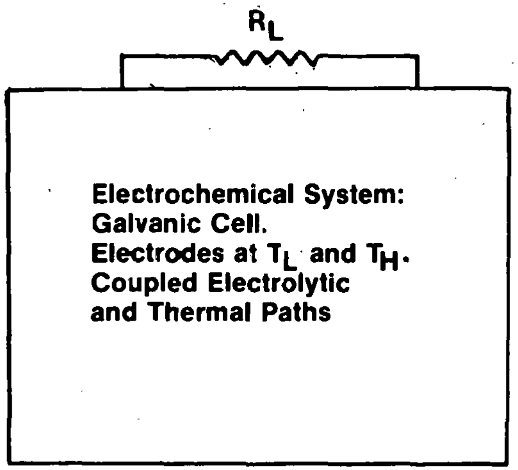
Electrochemical Cell 2 Reactions (Discharge)

$C \longrightarrow C^+ + e^-$ Anode

$A\text{-rich}(g) + e^- \longrightarrow A^-$ Cathode

$C + A\text{-rich}(g) \xrightarrow{T_H} CA$

Figure S-5. Coupled Thermal and Electrolytic Regeneration: Type 5



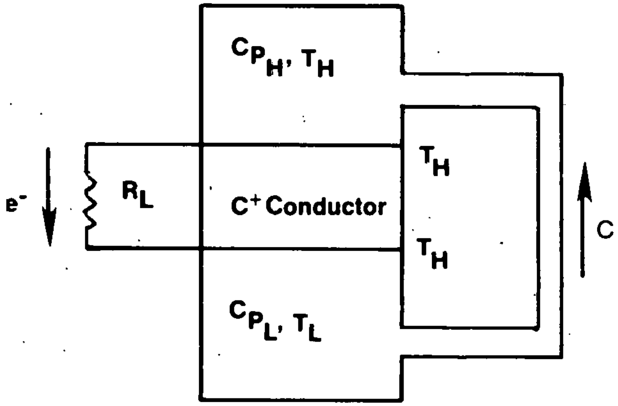
C |	C^+A^-	| C
Electrode at T_1	**(Solid or Liquid)**	**Electrode at T_2**

Electrochemical Cell Reactions

$$\left\{\begin{array}{ll} C \longrightarrow C^+ + e^- & \text{Anode } T_1 \\ C^+ + e^- \longrightarrow C & \text{Cathode } T_2 \end{array}\right.$$

If C = Metal, the roles of electrodes at T_1 and T_2 have to be reversed periodically.

Figure S-6. Coupled Thermal and Electrolytic Regeneration: Type 6



Electrochemical Cell Reactions	$C_{P_H,T_H}(g) \longrightarrow C^+_{P_H} + e^-$	Anode
	$C^+_{P_H} \longrightarrow C^+_{P_L}$	Ionic Conductor
	$C^+_{P_L} + e^- \longrightarrow C_{T_H,P_L}(g)$	Cathode
Cooling	$C_{T_H,P_L}(g) \longrightarrow C_{T_L,P_L}(l)$	
Pumping and Heating	$C_{T_L,P_L}(l) \longrightarrow C_{T_H,P_H}(g)$	

Figure S-7. Coupled Thermal and Electrolytic Regeneration: Type 7

Table S-1. EXAMPLES OF THE THERMALLY REGENERATIVE ELECTROCHEMICAL SYSTEMS

								Performance (cells at T_1)			
									Voltage at Current Density		
Type of Regeneration	System	Electrolyte	T_2 (°C)	T_1 (°C)	P (atm)	Carnot Efficiency (%)	Projected[d] Efficiency (%)	Open Circuit Voltage (V)	V (V)	I (mA/cm^2)	Comments
Type 1	LiH	eutectic molten, LiH-LiCl-LiF	900	530	1	32	-	0.6	0.3	200	Static cell; 0.025-cm vanadium diaphragm as H_2 electrode. Closed-loop system not tested.
Type 3 $T_2>T_1$	Na|Hg	molten NaCN:NaI:NaF 58:30:12 mol %	~685	~495	9	~20	~6	0.32	0.2	25	High resistivity of alumina matrix impregnated with electrolyte; total 1200-h operation of which 750 h were closed-loop operation.
Type 3	Na|Pb	molten NaF:NaCl:NaI 15.2:31.6:53.2 mol %	875	575	8/760	26	9-12	0.39	0.18	100	Complete system operated ~100 h. Regenerator only operated 1000 h.
Type 1 or 4 $T_2<T_1$	$Sn \rightarrow Sn^{2+}+2e^-$ $2Cr(III)-2e^- \rightarrow 2Cr(II)$	aqueous, excess Cl^-	20	80	-	-		~0.1	0.06	3[a]	Periodical power source.
Type 3 or 4	K|Tl	molten KCl	175	335	-	-	-	0.6	-	-	Regeneration by cooling and separating the two phases (liquid and solid).
Type 4 $T_2>T_1$	Na|NaCl|Cl_2	molten NaCl	-	827	-	-	-	3.24	I up to 4.3 A/cm^2 with IR drop only		Low coulombic efficiencies (40% Na utilization). Low electrode polarization on discharge at ~1000°C.
Type 4	Li|LiI|I_2	molten LiI	1170	500		50.6	~18	2.50	1.5	320	Closed-loop system not tested. Two mol % dissolved in LiI.
Type 4 $T_2>T_1$; $\Delta G_{T_2}<0$	$2UF_6 \rightarrow 2UF_5+2e^- + 2F^-$ $AsF_3+2e^- \rightarrow 2F^- + AsF_5$	solid electrolyte PbF_2(KF doped)	>900	25		-	-	-0.5(25°C) +0.3(900°C)	- -	- -	No voltage-current data.

Table S-1. EXAMPLES OF THE THERMALLY REGENERATIVE ELECTROCHEMICAL SYSTEMS (Concluded)

Type of Regeneration	System	Electrolyte	T_2 (°C)	T_1 (°C)	P (atm)	Carnot Efficiency (%)	Projected[d] Efficiency (%)	Performance (cells at T_1)			Comments
								Open Circuit Voltage (V)	Voltage at Current Density		
									V (V)	I (mA/cm^2)	
Type 5	I_2|molten alkali|I_2 metal iodides	molten electrolyte	350	350		-	~30	0.29	0.23	100	Cold finger at 25°C. Mass transfer problems.
Type 6	$I_2(T_1)$|α-AgI|$I_2(T_2)$	solid electrolyte α-AgI	340	184		25	~5[b]	0.2	0.1	1.4[a]	Internal resistance ~70 ohms; expected practical efficiencey 1%-2%.
Type 6	$Cu(T_1)$|$CuSO_4$|$Cu(T_2)$	aqueous acid	100	20		21	-	~0.09	0.03	8	Saturated solutions at each temperature.
Type 6	Pt|$Fe(CN)_6^{4-}$,$Fe(CN)_6^{3-}$|Pt	aqueous	80	30		14	-	0.08	-	-	Maximum power estimated <0.1 mW/cm^2.
Type 7	Na|β"-Al_2O_3|Na	solid electrolyte	800-900	100-200		~60	~25	~1.2	0.7	1000	Voltage losses due to interfacial polarization and thickness of β" alumina electrolyte.
Type 7	I_2|$PbI_2(\ell)$|I_2	molten PbI_2	170-400	20-100		-	-	0.17[c]	-	6.2[a,c]	Liquid electrolyte integrity difficult to maintain due to the pressure gradient.

[a] Current in mA.

[b] For T_2 = 500°C and T_1 = 200°C.

[c] T_2 enough to give 1 atm iodine; 24.5-ohm load; electrolyte temperature of 540°C.

[d] Some of the numbers in this column were obtained from a minimum amount of experimental data.

SECTION I

THERMAL REGENERATION: METAL HYDRIDES, HALIDES, OXIDES, AND CHALCOGENIDES

The general scheme for a thermally regenerative electrochemical system (TRES) (Type 1) is shown in Fig. S-1. It consists of an electrochemical cell in which substance CA is formed electrochemically from C and A at temperature T_L with production of electrical energy. The working substance CA is then heated and fed to the regenerator at temperature T_H, where it undergoes thermal decomposition into A and C. A cooling step completes the cycle, thus regenerating C and A at the lower temperature T_L.

$$\begin{array}{rlll} & C & \rightarrow C^+ + e^- & \\ \text{Electrochemical cell reaction at } T_L & A + e^- & \rightarrow A^- & \text{(I)} \\ \hline & C + A & \rightarrow CA & \\ \text{Heating} & CA\,(T_L) & \rightarrow CA\,(T_H) & \text{(II)} \\ \text{Thermal Regeneration at } T_H & CA & \rightarrow C + A & \text{(III)} \\ \text{Cooling} & C + A\,(T_H) & \rightarrow C + A\,(T_L) & \text{(IV)} \end{array}$$

This cycle can be considered a heat engine that converts part of the energy absorbed at a high temperature into useful work and rejects the remainder as heat at the lower temperature.

The maximum theoretical efficiency for reversible steps I and III and $\Delta C_p = 0$ is

$$\eta = \frac{\text{electrical work}}{\text{heat input}} = \frac{T_H - T_L}{T_H} \qquad (1)$$

The open-circuit voltage of the cell is

$$E = \frac{\Delta H_I}{nF} \; \frac{T_H - T_L}{T_H} \qquad (2)$$

where ΔH_I is the enthalpy of dissociation of CA into C and A at T_L.

The desirable thermodynamic properties for a regenerative electrochemical cell reaction are $\Delta G_I < 0$, $\Delta S_I < 0$, and ΔC_p as close to zero as possible. Thermodynamic criteria to judge the suitability of given chemical systems for regeneration at a given temperature (e.g., different classes of solar collectors) are complex. References addressing this question are given in Volume 2.

Basically, a thermally regenerative electrochemical cell of Type 1 should have the following properties:

- The regenerator temperature should be as high as possible for heat rejection purposes without stretching the materials limits. For nuclear heat sources, approximately 1000°C is a reasonable upper limit adopted by most investigators. For solar thermal sources, lower temperatures could be employed.
- The ΔG_{III} for the regeneration reaction should be small.
- The regeneration products should be easily separated and pumped, with the preferable situation being only two products (one gas and one liquid) and no solids.
- Electrochemical cell voltage should be high. Polarization losses should be kept to a minimum.
- The electrolyte should have low viscosity, high conductivity at the cell operating temperature, and a low melting point.
- The rate of dissociation at the regenerator should be high to keep the cell voltage constant under load.

TRES systems with strictly thermal regeneration can be further classified as involving single or multiple electrochemical reaction products and single or multiple regeneration steps. Major research efforts in each category are reviewed in this section.

I.1 SINGLE OR MULTIPLE ELECTROCHEMICAL REACTION PRODUCTS AND SINGLE-STEP REGENERATION

Such cells are commonly referred to as thermally regenerative fuel cells (TRFC) or thermally regenerative galvanic cells (TRGC).

I.1.1 Metal Hydride Systems: Lithium Hydride

The metal hydride systems were proposed as thermally regenerative electrochemical systems in 1958 as a result of the research performed at Mine Safety Appliance Research Corporation (MSA).

The lithium hydride system was the first to be envisioned as a practical TRES. The electrochemical cell reactions are:

$$\begin{array}{rl} Li(\ell) \rightarrow Li^+ + e^- & \text{anode} \\ 1/2\ H_2(g) + e^- \rightarrow H^- & \text{cathode} \\ \hline Li(\ell) + 1/2\ H_2(g) \rightarrow LiH & \text{cell reaction} \end{array}$$

This system is attractive because pure LiH decomposes at 900°C into easily separable liquid lithium and gaseous hydrogen. At this temperature the pressure of the hydrogen gas is about 760 mm Hg. The gas can be easily separated at this temperature because it diffuses very rapidly through metals (e.g., iron foil).

In the 10 years that followed the initial work on the metal hydride regenerative systems, emphasis was first placed on the porous gas electrodes. Since the electron transfer takes place in the vicinity of the electrode surface, three-phase contact sites must exist to achieve practical current densities. It was then recognized that this system provided an unusual opportunity to avoid the use of porous electrodes by using solid, thin foils of metals permeable to hydrogen gas at these elevated temperatures.

The regeneration step in the presence of the molten salt medium also proved less than straightforward. Low hydrogen partial pressures (100-200 Torr) for most of the molten salts tested forced the use of pumps to bring the hydrogen pressure to one atmosphere as required for better performance of the gas electrode. This further decreased the Carnot cycle efficiency.

The MSA experimental work included cell studies of Li, Na, K, and Ca electrodes with (a) LiCl-LiF (570°C), (b) LiCl-KCl (357°C), and (c) LiCl-NaCl-RbCl-CsCl (285°C) molten salt solutions as electrolytes. Other electrolyte systems also were investigated (KBr-KF-KI, LiCl-LiF-LiI, $LiBH_4$-KBH_4, and LiI-LiBr-KI-KBr). Continuous regeneration was attempted on cells, but severe materials and leakage problems were encountered. In general, due to the elevated temperatures employed, the porous electrodes tested (nickel, platinum, palladium, and carbon) exhibited variable catalytic activity at the surface of the frits, flooding of the frits with either hydrogen gas or fused electrolyte, concentration polarization, and severe corrosion. The diffusion membrane that was tested (Pd-Ag) corroded rapidly.

Initial studies at the TAPCO division of Thompson-Ramo-Wooldridge, Inc., (TRW) involved lithium and hydrogen reactants and a eutectic electrolyte mixture of LiCl-LiF (79:21 w/w %). At 510°C and 1 atm pressure, an open-circuit voltage (OCV) of 0.5 V at 6 mA/cm^2 could be obtained with a 50% polarization loss. An iron foil electrode was used. Major problems were encountered with melt, electrode and cell materials, and gases (argon and hydrogen). This led to high, spurious open-circuit voltages which decayed and to irreproducible results. Other metal foils studied include rhenium, nickel, zirconium, beryllium, tantalum, palladium, niobium, vanadium, rhodium, titanium, and thorium.

An investigation of the equilibrium pressure of hydrogen over the LiCl-LiF eutectic containing 5-10 mol % of LiH was performed at 880°C. At this temperature, appreciable vapor pressure of Li, which is insoluble in the melt, led to the recombination of evolved hydrogen and lithium, thereby forming LiH in the exit line.

A continuous thermal regeneration unit for a normal gravity environment was designed, fabricated, and tested with different pumping systems. The degree of regeneration achieved was lower than expected.

More extensive studies of the niobium foil cathode were carried out. A new lithium anode on porous niobium was developed. The cell potential was steady at 0.45 V OCV. Electrode polarization studies were carried out and indicated low cathodic and low anodic polarization. During these studies, current densities as high as 1500 mA/cm^2 at half of the OCV were achieved on a 0.012-cm foil. The current densities were later questioned by Argonne National Laboratory (ANL) researchers, who contended that the permeation would not support values of that magnitude.

From 1961 to 1967, the Chemical Engineering Division of ANL continued the research efforts on the lithium hydride TRES at a more basic level than that previously described. No attempt to develop a practical continuous regeneration cell was made, but guidelines for practical cell design were suggested. The performance of iron cells was tested in KCl-LiCl (41:59 mol %, 357°C) with an iron foil diffusion cathode. Spurious high voltages were encountered. The polarization of the lithium anode was found to be small. In agreement with TRW results, iron foils were found to support current densities less than 100 mA/cm^2.

Studies of the hydrogen diffusion through the diaphragm showed that the quantity of hydrogen diffusing through the metal is proportional to the difference in the square roots of the hydrogen pressures on each side, in agreement with earlier studies at TRW. The larger the pressure was at the cell, the higher was the output voltage.

The thermodynamic properties of lithium hydride were determined. Derived values of the standard free energy, enthalpy, and entropy at 527°C are $\Delta G_f^\circ = -6.74$ kcal/mol, $\Delta H_f^\circ = -20.9$ kcal/mol, and $\Delta S_f^\circ = -17.7$ cal/degree mol.

At ANL a practical batch cell was tested for 540 h at 535°C, giving current densities in excess of 200 mA/cm^2 at half of the OCV (i.e., 0.3 V). This cell used an untreated 0.025-cm-thick vanadium diaphragm and the LiH-LiCl-LiF molten salt. Preliminary practical cells also were tested with the lower-melting eutectic LiH-LiCl-LiI, which would result in larger Carnot cycle efficiencies due to the lower operating temperatures, and possibly in more effective regeneration.

Very little effort was spent on other alkali or other metal hydrides. Since the expected voltages for the higher-molecular-weight alkali hydrides are lower than that for lithium hydride, these systems were not pursued further. The lower decomposition temperatures for other metal hydrides suggest that some effort may be profitably invested in the renewed investigation of systems for lower-temperature applications that match solar sources.

I.1.2 Halide-Containing Systems

The use of metal halides as potentially interesting TRES has been suggested. In aqueous solution a galvanic cell with a cuprous bromide paste anode and a bromine gas electrode formed $CuBr_2$ electrochemically, with an OCV of 0.66 V. It was proposed that the regeneration could be achieved by heating and driving off water and bromine and returning the cuprous bromide to the cell anode. Most of the halide-containing systems investigated did not operate successfully.

I.1.2.1 Metal Iodides

The systems based on SnI_2, PbI_2, and CdI_2 were proposed by Lockheed Aircraft Corporation as potential TRES. The initial work was devoted to testing the performance of metal|molten iodide|iodine gas cells. When regeneration was attempted at temperatures up to 1000°C, no decomposition was observed. Later it was realized that these iodides are thermodynamically stable at these temperatures.

I.1.2.2 Mercury Halides and Systems Regenerated by Thermal Disproportionation Reactions.

Another system proposed by Lockheed was the cell: $Hg|HgBr_2{:}KBr$ (50:50 mol%) $|Br_2$ at 260°C. A calculated OCV of 0.61 V was expected, but under these conditions solid Hg_2Br_2 was formed due to the reaction

$$Hg(\ell) + HgBr_2(\ell) \rightarrow Hg_2Br_2(s)$$

An analogous system, using the disproportionation reaction of mercury(I) chloride as the thermal regeneration step, was proposed by the Illinois Institute of Technology Research Institute (IITRI) as a result of thermodynamic calculations:

$$Hg + HgCl_2 \underset{\text{thermal regeneration}}{\overset{\text{electrochemical cell}}{\rightleftarrows}} Hg_2Cl_2$$

I.1.2.3 Phosphorus Pentachloride

The system

$$PCl_3 + Cl_2 \underset{\text{thermal regeneration}}{\overset{\text{electrochemical cell}}{\rightleftarrows}} PCl_5$$

was proposed by Aerospace Corporation as thermally regenerative in organic solvents of high dielectric constant. A cell was built, but no significant results were reported.

I.1.2.4 Antimony Pentachloride

This is one of the many halide systems tested by IITRI from 1960 to 1967 as a result of theoretical thermodynamic calculations. This compound was selected because of its easy dissociation into liquid antimony trichloride and gaseous chlorine at relatively low temperatures. The drawback of this system is the expected poor ionic conductivity of the antimony chlorides. A solid electrolyte ($PbCl_2$ doped with KCl) was used in a small cell with some success.

The dissociation reaction $SbCl_5(\ell) \rightarrow SbCl_3(\ell) + Cl_2(g)$ was studied in detail. The regeneration was shown to work satisfactorily (dissociation of

80%-90% $SbCl_5$) over a wide range of temperatures (250°-350°C) and pressures (1-25 atm), producing liquid $SbCl_3$ and gaseous chlorine.

A unit with a formal power of 500 W was built with 10 cells connected in series. The anode and cathode compartment compositions were $SbCl_3:AsCl_3$ (2:1 mole ratio) and $SbCl_5:AsCl_3$ (4:1 mole ratio), respectively, both containing 4 w/w % $AlCl_3$. The cell had a regenerator unit and a heat exchanger between the electrochemical cell and the regenerator. The regenerator worked successfully, but the cell performance was very poor.

I.1.2.5 Hydrogen Halides and Other Halides

The hydrogen iodide thermally regenerative system was described in 1963. The fuel cell operated at 120°C with two porous platinized electrodes sandwiching the electrolyte, an aqueous solution of HI. The fuel cell reactions are hydrogen gas oxidation at the anode and iodine reduction at the cathode. The regeneration is performed by catalytic decomposition of HI at 1000°C. When the electrolyte was 43% H_2O and 57% HI at 120°C, the OCV was 0.5 V. Power output of 0.03-0.08 W/cm^3 at 75% thermal efficiency (the Carnot efficiency is 91%) seemed to be attained in this system with current densities as high as 100 mA/cm^2.

I.1.3 Oxide-Containing Systems and Other Systems

I.1.3.1 Sulfur Dioxide-Trioxide

In 1961-62, the system for which the regeneration reaction is

$$SO_3(g) \rightarrow SO_2(g) + 1/2\ O_2(g)$$

was investigated. The cell is $SO_2|\text{electrolyte}|O_2$. Thermodynamic studies of the regeneration steps indicated that at about 1000°C the sulfur trioxide is largely decomposed. Current densities were very low, and it was concluded that a thermally regenerative electrochemical system based on SO_2/SO_3 was not feasible. More recently, the investigation of this system in an alkaline medium was attempted.

I.1.3.2 Metal Oxides

From thermodynamic considerations, several metal oxide systems have been proposed, but they have not been studied experimentally. In the metal oxide fuel cells the lower-valent metal oxides are oxidized to the higher-valent metal oxides. The regeneration is performed by heat (see Sec. I.2.2.). Examples include Co, Cu, Mn, Pb, Fe, U, and groups VIA and VIB metals.

I.1.3.3 The System Sn|Sn(II),Cr(III),Cr(II)|C

In 1886, what appears to be the first thermally regenerative system was reported in the literature, based on the following reactions:

$$\mathrm{Sn} + 2\mathrm{Cr(III)} \underset{\text{thermal regeneration at } T_2 < T_1}{\overset{\text{electrochemical cell reaction at } T_1}{\rightleftarrows}} \mathrm{Sn(II)} + 2\mathrm{Cr(II)}$$

Electrical energy was produced periodically when a periodical temperature change was applied to the system. Thus, at a temperature of 90°-100°C the system delivered electrical energy, and at 15°-20°C it was chemically regenerated spontaneously.

The system is based on the galvanic cell composed of a tin anode and an inert cathode (e.g., porous graphite) reversible to the soluble species Cr(II) and Cr(III). At 90°-100°C the galvanic cell operates and generates electricity. When the reactants are exhausted, the regeneration is performed by disconnecting the electrical circuit and letting Cr(II) ions chemically reduce the Sn(II) ions to Sn metal, which deposits on the anode.

Almost a century later, Case's system was reinvestigated. The temperature dependence of the emf of the cell Sn|Sn(II)||Cr(III),Cr(II)|C, which changes sign between 25°-95°C, was measured at various electrolyte compositions ($\mathrm{HCl:CaCl_2}$). Low voltages (-60 to +60 mV) and low currents (~3 mA) were obtained.

I.1.4 Summary and Discussion of TRES Type 1

Table S-2 presents a summary of the thermally regenerative electrochemical systems investigated or proposed in the literature covered by Sec. I.1.

The majority of the systems reported in Sec. I.1 utilized molten-salt electrolyte systems and high regeneration temperatures (500°-1000°C). Several halide systems were shown not to decompose appreciably within the temperature range investigated. In some cases slow kinetics was responsible for the low decomposition yields. Catalytic decomposition was attempted only in the HI system. With the use of suitable catalysts, other systems may deserve renewed consideration. Very little experimental work has been done in oxide systems.

Aqueous and nonaqueous systems have received far less attention than molten salt media--principally because of the lower operating temperatures, which would not be suitable for coupling with nuclear heat sources but which certainly would be adequate for solar applications.

Systems operating at lower temperatures [analogous to Sn|Sn(II),Cr(III), Cr(II)|C], discovered by Case in the 19th century, have not been thoroughly

Table S-2. SUMMARY OF THERMALLY REGENERATIVE ELECTROCHEMICAL SYSTEMS INVOLVING METAL HYDRIDES, HALIDES, AND OXIDES

System (Electrochemical Reaction Products)	Medium	Electrochemical Cell Operating Temperature (°C)	Regeneration Temperature (°C)	Electrochemical Cell Performance	Regenerator Performance	Electrochemical Cell Problems	Regenerator Problems	Comments
LiH	Molten salts	300–550	>900	~60 $\mathrm{mW/cm^2}$ [a]	Low H_2 partial pressures	Gas electrode performance	Corrosion, solids on gas line	Ten years of research and development. No closed cell operated successfully.
$CuBr_2$	Paste of CuBr	--	--	~0.7 V[b]	Not attempted	—	Not attempted	Suggested system.
PbI_2;CdI_2;SnI_2	Molten iodide	~450	>1000	~17;~25;-- $\mathrm{mW/cm^2}$ [a]	Compounds are thermodynamically stable at 1000°C	—	—	These systems are not thermally regenerable.
Hg_2Cl_2	Molten salt	~200	~500	~0.7 V[b]	Poor	Self-discharge; high internal resistance	Separation of mercury vapors from gaseous $HgCl_2$	Diffusion of mercury vapor on gold and preferential absorption of $HgCl_2$ in NaCl/KCl were tried to separate the gases Hg and $HgCl_2$.
PCl_5	Organic solvents	~15	variable	0.28 V[b]	Poor	Reactions of P species with the solvent at 15°C accelerated at the solvent reflux temperature	--	--
$SbCl_5$	Molten $SbCl_5(AlCl_3)$ or solid electrolyte	~70	250-350	0.3 V[b]	Good; 80%-90% dissociation of $SbCl_5$	Low conductivity of antimony chlorides	—	Conductivity increases in mixtures of antimony and arsenic trichloride (OCV ~ 0.4-0.6 V), but cell resistances are still high.
HI	Aqueous	~120	1000	0.5 V[b]	Catalytic decomposition	--	—	Suggested system in the patent literature. Power output estimated to be 0.03-0.08 $\mathrm{W/cm^3}$ in a flow system.
SO_3	Molten salts or molten salts in organic solvents	~100-200	>1000	0.1-0.2 V[b]	No separation of $SO_2(g)$ and $O_2(g)$ obtained.	—	—	Very low current densities and low voltages.
Sn|Sn(II), Cr(III), Cr(II)|C	Aqueous	~90	~20	~60 mV	—	--	--	Periodic electricity source regenerated by cooling the system.

[a] Power at half of the open-circuit voltage.
[b] Open-circuit voltages.

investigated. This is an area in which existing thermodynamic data or new experimental data may indicate systems of better performance than Case's system.

I.2 MULTIPLE ELECTROCHEMICAL REACTION PRODUCTS AND MULTIPLE-STEP REGENERATION

A more complex galvanic cell has been devised in which there are two electrochemical reaction products (Type 2). The anode and cathode are composed of different compounds (e.g., metal halides or oxides). The anode and cathode are regenerated separately, generally at different temperatures. The general scheme of such a system for metal halides is as follows:

Galvanic Cell Reactions

$$MX_n + mX^- \longrightarrow MX_{n+m} + me^- \quad \text{anode}$$

$$M'X_{n'+m} + me^- \longrightarrow M'X_{n'} + mX^- \quad \text{cathode}$$

$$MX_n + M'X_{n'+m} \xrightarrow{T_1} MX_{n+m} + M'X_{n'} \quad \text{galvanic cell}$$

Regeneration Reactions

Anode regeneration: $MX_{n+m} \xrightarrow[T_2 > T_1]{\text{heat}} MX_n + m/2\ X_2(g)$

After separation of MX_n and X_2, MX_n is returned to the anode and X_2 is allowed to react with $M'X_{n'}$, thus regenerating the cathode.

Cathode regeneration: $M'X_{n'} + m/2\ X_2 \xrightarrow[T_3 < T_2]{T_3} M'X_{n'+m}$

These systems are clearly much more complex than those described in Sec. I.1. The general problem is whether the anode regeneration step produces two products in different physical states or not. For instance, if $SbCl_5$ or $CuCl_2$ are formed as a result of the anodic reaction, the regeneration yields $SbCl_3(\ell)$ or $CuCl(\ell)$ and $Cl_2(g)$, which can be separated by a relatively simple process (see Sec. I.1.2.4 for $SbCl_5$). However, if $SnCl_4$ or $TeCl_4$ are the result of the anodic processes at the thermal decomposition temperatures, the two products $SnCl_2$ or $TeCl_2$ and Cl_2 are in the gaseous state, and the difficult separation constitutes a very severe limitation for the practical application of this type of system. Self-discharge processes pose additional difficulties.

This approach to thermally regenerative galvanic cells was proposed and researched from 1960 to 1969 by IITRI.

I.2.1 Metal Halides

Cells involving metal halides selected from a large number of families were studied at IITRI during the 1960-67 period. Selected results are summarized in Table S-3.

The research on systems containing tin halides was abandoned because of the elevated decomposition temperatures of $SnCl_4$ (>1700°C), along with severe corrosion problems associated with $SnCl_2(g)$ and $Cl_2(g)$ at this temperature. In addition, there were problems in separating the two gaseous products. The system $TeCl_2$(anode)|$CuCl_2$(cathode) was considered the most promising, based on the galvanic cell performance (see Table S-2). A formally "5-kW" cell based on this concept was built and operated for about 30 minutes, after which leakages resulted in cell shutdown.

Though the galvanic cell studies indicated the feasibility of a $TeCl_2|CuCl_2$ cell, the demonstration of the ability of this system to undergo thermal regeneration was not successful. At the regeneration temperatures (>550°C) $TeCl_4$ decomposes into gaseous $TeCl_2$ and Cl_2, and several years of research were spent in trying to devise a suitable and efficient separation method.

I.2.2 Metal Oxides

The thermochemical and thermodynamic calculations performed at IITRI indicated a number of oxides with potential for thermal reversibility. Several were selected for practical cell tests in 1960. The cells gave low voltages (see Table S-4). Regeneration attempts were unsuccessful. The work on oxides was abandoned in favor of the halide systems, which seemed more promising (see Sec. I.2.1).

I.2.3 Discussion of TRES Type 2

This approach of multiple electrochemical reaction products and multiple-step regeneration (see Fig. S-2) is far more complex than the remaining types of TRES. To date, none of the systems investigated displayed both good cell performance and good regeneration performance. It is clear that most of the systems promising from an electrochemical point of view had a very poor regenerator performance if two gases were the result of the thermal regeneration. It is our feeling that systems of this type should be investigated only if the thermal decomposition products are in different physical states, or if major breakthroughs in the separation of gases are made in the near future.

Table S-3. THERMALLY REGENERATIVE ELECTROCHEMICAL SYSTEMS WITH TWO ELECTROCHEMICAL REACTION PRODUCTS INVOLVING THE REACTION OF METAL HALIDES

Reaction[a]	Composition		Temperature (°C)	Open-Circuit Voltage (V)	Voltage (V) Under Load of 100 ohms	Comments
	Anode	Cathode				
$SnCl_2+SbCl_5 \rightarrow SnCl_4+SbCl_3$	$SnCl_2:AlCl_3$ 50 w/w %	$SbCl_5:SbCl_3$[b]	150	0.47	0.3[b]	Stable performance for more than 2 weeks
$SnBr_2+SbBr_5 \rightarrow SnBr_4+SbBr_3$	$SnBr_2$	$SbBr_3+Br_2$[c]	Not given	0.15	--	Expected OCV of 0.54 V; low Br_2 concentration responsible for low OCV
	Mole Fraction (in $AlCl_3$)					
$SnCl_2+2CuCl_2 \rightarrow SnCl_4+2CuCl$	0.23	0.25	205	0.70	0.29	Platinum electrodes
$CuCl+CuCl_2 \rightarrow CuCl_2+CuCl$	0.31	0.25	253	0.25	0.11	Platinum electrodes
$TeCl_2+2CuCl_2 \rightarrow TeCl_4+2CuCl$	1	0.25	205	0.92	0.51[d]	Platinum electrodes
$HgCl+CuCl_2 \rightarrow HgCl_2+CuCl$	0.40	0.25	200	0.75	0.26	Platinum electrodes

[a] 1st reactant: anode; 2nd reactant: cathode.

[b] In $AlCl_3:KCl$ eutectic; load: 10,000 ohms; current density: 50 mA/cm^2.

[c] In $AlBr_3:KBr$ eutectic.

[d] Current densities: 22 mA/cm^2 for 9-mm electrolyte thickness; current density increases with decreased electrolyte thickness and in flow operation.

Table S-4. THERMALLY REGENERATIVE ELECTROCHEMICAL SYSTEMS WITH TWO ELECTROCHEMICAL REACTION PRODUCTS INVOLVING THE REACTION OF METAL OXIDES

	Composition in Molten Eutectic $Li_2CO_3:Na_2CO_3$[a]		emf (V)		Resistance
Cell	Anode	Cathode	Calcd	Measured	(ohms)
$MnO \mid CO_3^{2-} \mid Sb_2O_5$	80 wt % MnO	80 wt % Sb_2O_5	0.29	0.17	2800
$MnO \mid CO_3^{2-} \mid Sb_2O_5$	same as above with 30 vol % graphite added		0.29	0.27	29
$Cu_2O \mid CO_3^{2-} \mid Sb_2O_5$	Graphite added		0.30	0.23	2000

[a] Electrolyte: 80 wt % ZrO_2; 20 wt % eutectic $Li_2CO_3:Na_2CO_3$.

SECTION II

THERMAL REGENERATION: ALLOYS OR BIMETALLIC SYSTEMS

A schematic representation of a thermally regenerative alloy system is shown in Fig. S-3 (Type 3). Liquid metal C is oxidized to the respective ion C^+ at the anode. These ions migrate into the C^+ conductor electrolyte and undergo reduction and solubilization in B or alloy formation [C(B) or C_xB_y] at the cathode. This alloy alone or combined with anode material is pumped (e.g., electromagnetically) or flows to a boiler where it is heated above the boiling point of the metal of lower boiling point. In a separator the vapor phase, richer (not necessarily pure) in the more volatile component, is separated from the liquid phase, richer in the less volatile metal, and the two streams are individually returned to the galvanic cell. Therefore, the electrochemical reaction product is a liquid metal alloy [C(B)] or an intermetallic compound (C_xB_y) in a concentration cell with respect to the electroactive species C^+/C.

Most of these cells employed molten salt electrolytes due to the high conductivity of these media ($\sim 10^{-1}$–10 ohm^{-1} cm^{-1}) compared to that of aqueous electrolyte solutions ($\sim 10^{-4}$–10^{-2} ohm^{-1} cm^{-1}), and because of the high exchange currents obtained at metal electrodes due to small activation polarization. The major voltage losses in this type of cell are ohmic.

Many of the important parameters in selecting a bimetallic system for feasible thermal regeneration are implicit in the phase diagram of the system. Compound formation in the cell is desirable to lower the activity of C^+ at the cathode and thus increase the obtainable voltage. However, for thermal regeneration, the melting point of such compounds should not be so high that separation of the vapor/liquid region from the liquid/solid region cannot be achieved at a practical operating pressure.

II.1 AMALGAM AND THALLIUM CELLS

II.1.1 The Potassium-Mercury System

The electrochemical and regenerative feasibility of the system K/Hg was investigated by the Allison Division of General Motors Corporation (GMC). The liquid metal cell employed was $K(a_1)(Hg)|KOH\text{-}KBr\text{-}KI|K(a_2)(Hg)$, where the electrolyte composition of 70:15:15 mol % of KOH:KBr:KI, respectively, is molten at 250°C.

Several cell configurations were employed. For batch operation, a differential density cell held within a ceramic crucible was built with the K/Hg amalgam on the bottom, the ternary melt floating on top of the amalgam layer, and finally, a layer of molten potassium floating on top of the electrolyte. In the tests performed with flow cells, the mode of operation was not fully thermally regenerative because the liquid potassium was fed from a tank. The potassium-enriched mercury from the boiler was stored, and the mercury-enriched vapor from the boiler was condensed and fed to the cathode. Fresh mercury supply was furnished from time to time.

The results obtained at GMC showed that the K/Hg system is electrochemically simple, with the possibility of generating current densities of the order of 100 mA/cm^2 at ca. 0.5 V with relatively low self-discharge rates. Some mechanical problems of the cell were leakage through the seals, electrolyte leakage out of the matrix due to pressure differences between anode and cathode compartments, and cracking of the matrix. One advantage of the liquid metal cell for high current density operation, when the temperature inside the cell can rise appreciably, is the ease of heat management in the system due to the flow operating conditions and the inherent excellent heat transfer capabilities of these metals. Closed-loop operation, however, has not been demonstrated.

II.1.2 The Sodium-Mercury System

A thermally regenerative alloy cell system called TRAC was developed at Atomics International, a Division of North American Aviation, Incorporated (presently Rockwell International). The mission of the program was to investigate the feasibility of closed-cycle, static devices for converting heat into electricity based on liquid metal amalgam cells with the sodium-mercury system. Most of the research aimed at high power output/weight devices--not the highest possible efficiency of the system. Operating temperatures for the cell of ~460°-510°C and for the regenerator of 670°-700°C were imposed, thus allowing a maximum Carnot efficiency of the order of 20%. The actual efficiency is reduced to about half of that value because of irreversibilities and was reduced further by weight constraints to about 30% of the Carnot efficiency.

II.1.2.1 Batch Cells

The sodium-mercury amalgam cell $Na(a_1)(Hg)|NaCN\text{-}NaI\text{-}NaF|Na(a_2)Hg$ employed by Atomics International contained amalgams of different sodium activities in the anode and cathode compartments, which were separated by a porous (40%-50% porosity) beryllium oxide matrix impregnated with the ternary salt mixture of eutectic composition 58:30:12 mol % of NaCN:NaI:NaF, respectively, which was molten at 477°C.

II.1.2.2 Flowing Electrode Cell and Closed-Loop Operation

A flowing electrode TRAC cell was built and coupled with the regeneration loop. The liquid stream from the condensing radiator is nearly pure mercury, which, if the radiator temperature is ~480°C, fixes the system pressure at about 6 atm. The pressure in the separator will be very nearly the same as the cell inlet pressure. With the pressure and temperature at the separator fixed, the sodium content in the liquid and vapor phases is determined by the equilibrium values under these conditions. The separator was designed as a centrifugal cyclone. Equilibrium between liquid and vapor is approached in the separator, and a one-theoretical-plate separation should occur (this was verified under operating conditions). It was concluded that at 685°C the vapor phase is nearly pure mercury with 0.1-1 atom % sodium (cathode stream), whereas the liquid phase is approximately 36 atom % sodium (anode stream).

A maximum OCV of about 0.25 V was developed, but the system operated satisfactorily, with the cell internal resistance remaining essentially constant. The loop performance was steady, but the pressure drop across the loop increased after 118 hours. The matrix was intact (dark colored), but excess electrolyte was found in the cell. The sealing gaskets had been corroded by atmospheric oxygen from the outside. The loop contained loose black material which was found to be iron. The buildup of materials in the loop and the excess electrolyte were believed responsible for the pressure drop increase during the test.

A second test was carried out until the system failed. The cell temperature was maintained at ~495°C and the system pressure was maintained at 9.2 atm. A maximum steady OCV of 0.32 V was achieved. The cell operated continuously for about 1200 hours, during which the cell internal resistance remained constant. The maximum power density generated was 5 mW/cm^2 from 25 mA/cm^2 at 0.2 V. The power and current densities were low as a result of a high resistivity of the electrolyte-matrix (54 ohm cm) caused by the low porosity (15%) of the alumina tube employed.

These tests demonstrated the compatibility of the alumina matrix with the sodium amalgam, although beryllium oxide was found to be a better material, presenting higher resistance to alkali metals and their amalgams and having higher thermal conductivity than magnesia or alumina. There was no leach of a detectable amount of electrolyte out of the matrix during about 500 hours. Cell materials do not seem to pose a problem to long-lived devices.

II.1.3 The Potassium-Thallium and Analogous Systems

A different approach for the regeneration in the alloy systems has been suggested in the literature. A galvanic cell of the type $C(a_1)Tl|$molten electrolyte$|C(a_2)Tl$ operates at a temperature above the melting point of the alloy. The streams of the alloys from the anode and cathode are combined, well mixed, and cooled down to a definite temperature (partially solidifying), which ensures optimum separation of a C-metal-rich phase and a C-poor phase, one of which will be in the solid state and the other in the liquid state. These two phases can be mechanically separated by conventional methods and the two streams of regenerated anode and cathode materials individually reheated to the cell temperature and returned to the galvanic cell.

A system that seems suitable for this type of regeneration is composed of potassium and thallium. The galvanic cell $K(Tl)a_1|K^+|K(Tl)a_2$ consists of a molten K-Tl solution rich in K as anode and a molten K-Tl solution rich in Tl as cathode, separated by a porous matrix impregnated with molten KCl at an operating temperature higher than 335°C. Approximately 0.6 V (OCV) has been obtained with a cell of this type.

II.2 BIMETALLIC CELLS

II.2.1 Sodium-Containing Systems

II.2.1.1 The Sodium-Tin System

Laboratory cells of the type Na|Na^+ glass or molten salt|Na_xSn were investigated at the Allison and Delco-Remy Divisions of GMC. The cathode composition was varied between 15 and 30 mol % of sodium, and the resulting OCV were 0.42-0.36 V (500°C) and 0.43-0.33 V (700°C).

Static and flowing cells were used to study charge-discharge behavior of these cells. No concentration polarization effects were found in these studies. Problems of short circuit in the flowing cells were found and attributed to flooding of the porous alumina matrix with sodium. A less porous matrix impregnated with the molten eutectic probably would allow a maximum OCV of 0.5 V and ~700 mA/cm^2 at 0.25 V.

At the Allison Division the ability of this sytem to undergo thermal regeneration up to temperatures of ~1000°C was investigated. It was found that only above 1100°C could 200-400 Torr of sodium vapor pressure be obtained, facilitating the thermal regeneration. One attempt was made to run in a regenerative mode using the cell Na|NaI-NaCl impregnated alumina|Na_xSn at 625°-650°C and the regenerator at 1000°C. The system did not accomplish regeneration at 1000°C.

II.2.1.2 The Sodium-Lead System

The galvanic cell Na|NaF-NaCl-NaI|Na_xPb was chosen by ANL as a possible thermally regenerable system, with the eutectic electrolyte of composition 15.2:31.6:53.2 mol % of NaF:NaCl:NaI, respectively, molten at 530°C.

The emf of sodium-lead cells is 0.3-0.5 V (alloy composition ~10-40 atom % of sodium). One complete cell and regenerator system was operated for approximately 100 hours. The regenerator was operated to distill sodium to be consumed at the cell anode. Eleven runs of 2 to 7 hours were performed for a total operating time of 45 hours. The cell operated at 545°-600°C and at 5.7-9 Torr pressure.

Cell OCVs as high as 0.41 V at 575°C were recorded, indicating that the regenerator had reduced the cathode sodium concentration from 30 to 18 atom %. Several design concepts were proposed, including designs for multicell operation. Due to the low voltages obtained per cell, a practical device would have to connect many cells in series to achieve useful voltages. The efficiency of this system should range between 9% and 12%. This system was not considered attractive for a practical device.

II.2.1.3 The Sodium-Bismuth System

The cell Na|NaF-NaCl-NaI|Na_xBi also was investigated at ANL with the ternary eutectic electrolyte described in the Na/Pb system above (Section II.2.1.2). The sodium-bismuth cell generated emfs in the range of 0.55-0.75 V, ca. 0.2 V higher than the Na/Pb cells, thus promising a better performance. A differential density cell was operated at 550°C with electrolytic, rather than thermal, regeneration for a period of 17 to 18 months without deterioration of performance. The OCV of this cell was 0.7 V (20 atom % sodium in the cathode), and the current densities on discharge of 90 and 110 mA/cm^2 were obtained at 0.5 and 0.45 V, respectively. No decomposition of the molten salt was observed, and minimum corrosion was detected after this period. One drawback of these cells is the relatively fast self-discharge associated partly with the large solubility of the intermetallic compounds (e.g., Na_3Bi) in the molten salt system, which increases with temperature.

However, to design a regenerative sodium-bismuth system, the operational pressure has to be $\geq$240 Torr. To collect pure sodium at this pressure, a condenser temperature of approximately 770°C is required and would raise the galvanic cell operating temperature by about 270°C. Another consequence of operating at 240 Torr is that in order to obtain a reasonable cathode composition, the regeneration temperature should be from 1200° to 1300°C. At this temperature, materials problems and dynamic corrosion by Na/Bi could be very difficult to overcome.

II.2.2 Lithium-Containing Systems

The systems Li/Sn, Li/Bi, Li/Te, Li/Cd, Li/Zn, and Li/Pb were investigated at ANL in the 1961-67 period, considering both electrolytic and thermal regeneration. Emf data for these systems were obtained using as an electrolyte the binary eutectic LiF-LiCl or LiCl-KCl molten salts at approximately 500°C. For thermal regenerative operation, both the Li/Bi and Li/Te systems were found inadequate because of the high vapor pressure of Bi and Te over their respective lithium solutions. Only Li/Sn was attractive for thermal regeneration operation because of the very low tin vapor pressures over lithium-tin alloys, even at very high temperatures (e.g., 1200°C).

The lithium vapor pressure over cathodes of reasonable composition (e.g., 30 atom % lithium) is of the order of 2 Torr. The regeneration at this low pressure may pose additional problems in terms of heat, mass, and momentum transfer, besides the materials and corrosion problems of operating the thermal regeneration at 1200°C. However, since the cell could operate with a ternary eutectic LiCl-LiF-LiI of melting point <350°C, the expected Carnot efficiency for this system could be 58%, and a much higher net efficiency could be expected (25% to 30%) if the materials problems can be overcome.

II.3 SUMMARY OF THE PERFORMANCE AND DISCUSSION OF THERMALLY REGENERATIVE ALLOYS OR BIMETALLIC SYSTEMS

Table S-5 assembles results for the alloy and bimetallic systems reported in our review. It is fair to state that the electrochemical cell performances

Table S-5. SUMMARY OF THERMALLY REGENERATIVE ALLOY OR BIMETALLIC SYSTEMS IN MOLTEN SALT MEDIUM

System	Electrochemical Cell Operating Temperature (°C)	Regeneration Temperature (°C)	Electrochemical Cell Performance	Regenerator Performance	Electrochemical Cell Problems	Regenerator Problems	Comments
K/Hg	250	350	50-100 mW/cm^2	Not tested 100%	Concentration polarization; ohmic losses on matrix-electrolyte	--	Regenerator pressure ~1 atm. Only partial regeneration achieved. Potassium enriched amalgam fed from a tank.
Na/Hg	~495	~685	5 mW/cm^2	Performed well for ~700 h	Ohmic losses on matrix-electrolyte	--	35 mW/cm^2 achieved in flow cells. Regenerator pressure ~9 atm. Materials compatibility demonstrated for >500 h. Closed-loop operation demonstrated.
K/Tl	335	~175	0.6 V OCV	Not attempted	--	--	0.5 mole fraction Tl in the anode and 0.8 mole fraction Tl in the cathode achieved by cooling at 175°C. No closed-loop operation demonstration.
Na/Sn	~650	~1000	30 mW/cm^2	15 min	--	Corrosion of metal to ceramic seals by hot sodium vapor	Better regeneration at ~1200°C, but more materials problems.
Na/Pb	575	875	~20 mW/cm^2	One regenerator design operated cell 1000 h	--	--	Complete cell regenerator operated ~100 h closed-loop. Regenerator pressure of 8 Torr.
Na/Bi	565	~1200-1300	50 mW/cm^2	Not attempted	--	Materials problems at 1200°C	Regenerator pressure should be ~240 Torr.
Li/Sn	~400	~1200	--	Not attempted	--	Materials problems at 1200°C; heat, mass and momentum transfer	Regenerator pressure of 2 Torr.

listed in the table are low limits. These systems exhibited better cell performance in batch cells tested. They are also good storage battery systems. The coupling of the electrochemical cell and regenerator system was successful in the Na|Hg and Na|Pb systems. The operating temperatures were very high because of the application envisioned at the time. One can safely state that these systems were closer to success in the thermal regeneration mode than those described in Secs. I.1 and I.2, when compared for regeneration in the >500°C temperature range. Since the cell reactions $C \rightleftarrows C^+ + e^-$ are reversible, the systems of high coulombic efficiency (e.g., Na|Hg and Na|Pb) should be suitable for operation in the coupled thermal and electrolytic regeneration mode. A more detailed integral systems analysis could be performed to suggest suitable systems to reinvestigate once a solar-derived, high temperature source is identified. This analysis is particularly important in view of the large quantities of materials pumped.

At this point it should be emphasized that past investigation of concentration cells for power generation purposes in media other than molten salts is rather limited. The reasons are the generally slow electrode kinetics in other media and high ohmic losses due to lower conductivity. Molten salts with lower melting points and other media could be the basis for the investigation of other thermally or coupled thermal and electrolytic regeneration systems.

SECTION III

THERMOGALVANIC OR NONISOTHERMAL CELLS

Thermogalvanic cells (Type 6) (also called thermocells) can be defined as galvanic cells in which the temperature is not uniform. They are the electrochemical equivalent of thermoelectric devices, which also convert heat directly into electricity. In these cells two or more electrodes are at different temperatures. These electrodes, not necessarily chemically identical or reversible, are in contact with an electrolyte, solid or liquid, not necessarily homogeneous in composition, and with or without permeable membranes interposed in the electrolyte. During the passage of current through the thermogalvanic cells, matter is transferred from one electrode to the other as a result of the electrochemical reactions at the electrode/electrolyte interface and ionic transport in the electrolyte. In this respect, the thermogalvanic cell differs from metallic thermocouples, or thermoelectric devices in general, in which no net transfer of material occurs and the state of the conductor remains unchanged with the passage of current.

The emf of a thermogalvanic cell in its initial state arises from three factors: (1) the differences in electrode temperature, (2) the thermal liquid junction potential, and (3) the metallic thermocouple effect. In general, the emf arising from (1) and (2) is about two orders of magnitude larger than that arising from (3) at the junction in the external circuit between two electrode metals at different temperatures (the Seebeck effect). With the passage of time, a thermocell is subject to thermal diffusion in the electrolyte (Soret effect), which will tend to concentrate the more concentrated electrolyte in the cold region. The concentration gradient further changes the two electrode potentials, and the cell reaches a new stationary state (final emf). The formation of the concentration gradient can be avoided by stirring or convection (as long as the thermal gradient is not destroyed), and it is not present in the case of solid electrolytes in which only one kind of ion is mobile.

The thermogalvanic cell can be written as

$$M(T_1)|\text{electrode}(T_1)|\text{electrolyte}(T_1)|\text{electrolyte}(T_2)|\text{electrode}(T_2)|M(T_1)$$

where $T_2 > T_1$. The temperature T_1 is fixed and T_2 is varied. The most widely used sign convention for thermogalvanic cells is that the emf (E) is positive when the terminal connected to the electrode at T_2 is positive with respect to that connected to the cold electrode. Therefore, the hot electrode is the cathode, and $(dE/dT_2)_{T_1}$ is positive. The coefficient $(dE/dT)_{\text{thermal}}$ is the thermoelectric power, sometimes also designated the Seebeck coefficient by analogy with the nomenclature used in thermoelectric phenomena. The thermoelectric power is measured at open circuit ($I = 0$).

The efficiency of the thermogalvanic cells is related to the Carnot cycle efficiency. However, since the thermal and electrolytic paths are not separated, the maximum efficiency is only a fraction of the Carnot efficiency. It depends on the thermal and electrical conductivities, as well as on the thermoelectric power (no load). Under load, polarization effects that effectively decrease the power outputs obtainable should also be included. The performance of some of the thermogalvanic cells developed for power generation is summarized in Table S-1.

III.1 MOLTEN SALT THERMOGALVANIC CELLS

A variety of molten salt thermocells with solid, liquid, and gaseous electrodes have been studied. The thermoelectric powers of several examples of molten salt thermogalvanic cells are assembled in Tables S-6, S-7, and S-8. Thermoelectric powers of 0 to 1.5 mV/degree are found over a wide range of temperatures and materials. Efforts to develop practical devices have been minimal (e.g., $Cl_2|$molten $NaAlCl_4|Cl_2$). These devices give low voltages.

III.2 THERMOGALVANIC CELLS WITH SOLID ELECTROLYTES

Table S-9 lists thermoelectric powers for some thermocells with solid electrolytes. Comparison of Table S-9 with Tables S-6, S-7, and S-8 indicates that for the same salt system the thermoelectric powers increase in the order: $M|MX(\ell)|M < X_2|MX(\ell)|X_2 \approx M|MX(s)|M < X_2|MX(s)|X_2$, thus reflecting the larger homogeneous thermoelectric powers in the solid salts as compared to the molten salts.

The Thermogalvanic Cells $Ag|\alpha\text{-}AgI|Ag$ and $I_2|\alpha\text{-}AgI|I_2$

Thermocells involving the systems $Ag|\alpha\text{-}AgI|Ag$ and $I_2|\alpha\text{-}AgI|I_2$, the "silver cell" and the "iodine cell," respectively, were developed at the General Electric Company in the sixties.

Several cell configurations were tried for the silver thermocell, such as silver electrodes sandwiching the α-AgI electrolyte (ionic resistivity of 0.38 ohm cm at 500°C; 0.47 ohm cm at 350°C). During operation, silver is dissolved from the hot anode, silver ions migrate from the hot to the cold electrode, and finally, silver metal is deposited at the cold electrode. The problem of dendrite formation in these cells leads to loss of contact at the electrode/electrolyte interface, loss of silver, and short circuit of the cell. The cells need a provision for reversing the hot and cold sides for continuous operation. Current-voltage curves were obtained for these cells. For instance, for $\Delta T = 226°C$, a thermopotential of ~0.13 V OCV was observed, and at ~0.05 V a current of 40 mA was drawn from the cell ($R = 1.6\ \Omega$).

The obstacles mentioned for the silver cell did not appear in the iodine cell, due to the gaseous electrode. The iodide ions are oxidized at the cold electrode to iodine, producing an increased iodine pressure at the cold electrode. Silver ions migrate from the cold to the hot electrode, where iodine is reduced with the formation of silver iodide. Some of the major problems of this cell were contraction of the AgI on heating, the maintenance of the three-phase electrode/electrolyte/iodine interface, and encapsulation. The discharge characteristics of laboratory cells were studied as a function of temperature. At $\Delta T = 280°C$ electrochemical polarization limits the current drain, but at $\Delta T < 170°C$ mostly IR (ohmic) polarization is observed.

Table S-6. SUMMARY OF THERMOELECTRIC POWERS IN Ag|MOLTEN SALT|Ag THERMOCELLS

Molten Salt	Temperature (°C)	$(dE/dT)_{I=0}$ (mV/degree)
Nitrates		
$AgNO_3$	305	-0.344
$AgNO_3$:$NaNO_3$(0.5:0.5)[a]	310	-0.331
$AgNO_3$:$NaNO_3$(0.05:0.95)[a]	310	-0.419
$AgNO_3$:$NaNO_3$(0.5:0.5)[a]	310	-0.328
$AgNO_3$:$LiNO_3$(0.1:0.9)[a]	310	-0.496
$AgNO_3$:$LiNO_3$(0.5:0.5)[a]	310	-0.379
Halides		
AgCl	450	-0.40
AgBr	477	-0.45
AgI	577	-0.50
Sulfate		
Ag_2SO_4	657	-0.31

[a] Mole fraction composition.

Table S-7. SUMMARY OF INITIAL THERMOELECTRIC POWERS IN METAL|MOLTEN SALT|METAL THERMOCELLS

Cell	Temperature (°C)	$(dE/dT)_{I=0}$ (mV/degree)
Cu|CuCl|Cu	462-588	-0.436
W:Pb(ℓ)|$PbCl_2$|Pb(ℓ):W	500-700	-0.006
W:Pb(ℓ)|$PbBr_2$|Pb(ℓ):W	400-700	-0.040
Pb(ℓ)|$PbCl_2$|Pb(ℓ)	627	-0.008
Pb(ℓ)|PbI_2|Pb(ℓ)	627	-0.048
Zn|$ZnCl_2$|Zn	327	+0.13
Sn|$SnCl_2$|Sn	--	-0.028

Table S-8. SUMMARY OF THERMOELECTRIC POWERS IN X_2|MOLTEN SALT|X_2 THERMOCELLS

Cell	Temperature (°C)	$(dE/dT)_{I=0}$ (mV/degree)
$Cl_2 \mid AgCl \mid Cl_2$[a]	500-900	-0.65
$Cl_2 \mid LiCl \mid Cl_2$[a]	627	-0.534
$Cl_2 \mid NaCl \mid Cl_2$	827	-0.483
$Cl_2 \mid KCl \mid Cl_2$	830-950	-0.40
$Cl_2 \mid KCl \mid Cl_2$	727	-0.504
$Cl_2 \mid PbCl \mid Cl_2$	727	-0.544
$Cl_2 \mid CsCl \mid Cl_2$	727	-0.533
$Cl_2 \mid KCl{:}LiCl \mid Cl_2$ (54.5 wt % KCl)	500-900	-0.55
$Cl_2 \mid NaAlCl_4 \mid Cl_2$	--	-1.0 to -1.4
$I_2 \mid PbI_2 \mid I_2$	627	-0.637
$I_2 \mid LiI \mid I_2$	627	-0.595

[a] One atm of Cl_2 pressure.

Table S-9. SUMMARY OF THERMOELECTRIC POWERS IN SOLID ELECTROLYTE THERMOCELLS

Cell	Temperature (°C)	$(dE/dT)_{I=0}$ (mV/degree)
$Ag \mid AgI(s) \mid Ag$	140-500	0.60
$Ag \mid \alpha\text{-}AgI \mid Ag$	150-400	0.56-0.60
$Cl_2 \mid AgCl(s) \mid AgCl_2$	300-410	1.29
$Cl_2 \mid \alpha\text{-}AgI \mid Cl_2$	160-500	1.2-1.4
$Pb \mid PbCl_2(s) \mid Pb$	200-470	0.54
$Cl_2 \mid PbCl_2(s) \mid Cl_2$	260-400	1.28
$Pb \mid PbBr_2(s) \mid Pb$	350	0.40
$Br_2 \mid PbBr_2(s) \mid Br_2$	320	1.20

The efficiency of the iodine cell is improved by reversing the temperature gradient to avoid the advance of the solid electrolyte from the high-pressure zone. The thermoelectric powers obtained, 1.2-1.4 mV/degree, compare well with the theoretical values of 1.3-1.5 mV/degree. The efficiency of this system, calculated by using solid-state thermoelectric efficiencies expressions, was ~5%.

III.3 THERMOGALVANIC CELLS IN AQUEOUS AND NONAQUEOUS SOLVENTS

The work described in this section was aimed at power generation. The power output and voltage of some thermocells have been measured (e.g., $Cu|CuSO_4$ in $H_2O|Cu$ and $Cu|CuSO_4$ in $H_2O + 20\%\ H_2SO_4|Cu$). The voltages attained at maximum power were 31 and 28 mV, which correspond to powers of 0.03 and 0.25 mW/cm^2, respectively. Due to mass transfer occurring when the cell is operating under current drain conditions, Cu is dissolved (oxidized) at the cold electrode and deposited at the hot electrode, and therefore Cu^{2+} ions are transferred from the cold to the hot electrode. In order to draw power continuously from the cell, it is necessary to reverse the process and heat the cold electrode and cool the hot electrode by some mechanical means. The growth of dendrites and the loss of copper are the major problems anticipated for long-term operation.

Thermogalvanic cells in which the two redox species are soluble have been investigated at Battelle-Geneva. In these cells the permanent mass transfer problems associated with metal deposition are not present; however, the discharge behavior of these cells showed that concentration polarization, i.e., the rate of mass transfer of the electroactive species [Fe^{3+}, Fe^{2+} or $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$] to the electrode limits the current and therefore the power output of such devices. Powers of the order of <0.05 mW/cm^2 (Fe^{3+}, Fe^{2+}) to <0.1 mW/cm^2 [$Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$] have been obtained.

Sulfuric Acid Concentration Thermogalvanic Cell

A sulfuric acid cell in which the two platinum electrodes sandwich a porous nonconducting barrier has been investigated. Heat is applied at the hot electrode, and water is evaporated from the heated portion and condenses at the cold electrode. Therefore, the solution adjacent to the cold electrode will be more dilute than that adjacent to the hot electrode. Capillary action in the porous barrier compensates for the loss of water and sulfuric acid as the hot part dries out, so that at equilibrium, a balance between these two processes is achieved. Since the activity of acid and water in sulfuric acid solutions varies widely with composition and also with temperature, this cell is a concentration cell on which the smaller thermogalvanic effect is superimposed.

OCV as high as 0.7-0.8 V were achieved and the maximum power output was 17 mA/cm^2 at 0.5 V. A cell was tested continuously for 18 hours under load with no deterioration of performance.

III.4 DISCUSSION OF TRES TYPE 6

Table S-1 presents the results for some of the thermogalvanic cells developed for power generation. Molten salt thermocells can, in principle, give more power due to the higher range of liquidus in which they exist. However, some data exist for aqueous media to indicate that modest powers of ~100 $\mu W/cm^2$ can be achieved in these systems. In view of the availability of solar heat sources for temperatures less than 100°C (e.g., solar ponds), the investigation of these low-temperature, modest-power, relatively inexpensive engines should be continued. Research in this area is being performed at SERI.

SECTION IV

COUPLED THERMAL AND ELECTROLYTIC REGENERATION BASED ON PRESSURE DIFFERENCES OF THE WORKING ELECTROACTIVE FLUID

IV.1 SINGLE CELLS

The electrochemical heat engines (Type 7) described in this section are based on pressure differences of the working electroactive fluid across the isothermal electrolyte (solid or liquid) (see Fig. S-7). The pressure difference is maintained by using the changes in the vapor pressure with the temperature of the working electroactive fluid. The work performed is equivalent to an isothermal expansion of the working electroactive fluid from pressure P_H to P_L at temperature T_H through the electrolyte and its interfaces. After expansion, the working fluid is condensed in a cold reservoir and can be recycled to the high temperature, high pressure part of the cell by means of a pump. These cells are basically concentration cells. If the temperature across the electrolyte remains constant, one of the sources of irreversibilities is minimized. One of the major advantages of this concept is that no chemical regeneration step is necessary. Because the working fluid does not undergo chemical changes, no regeneration and separation steps are necessary.

At open circuit the voltage of these engines is given by the Nernst equation as

$$V_{OC} = \frac{RT_H}{nF} \ln\left(\frac{f_H}{f_L}\right) \qquad (1)$$

where f = fugacity of the working fluid at the high pressure electrode (f_H) and at the low pressure electrode (f_L).

IV.1.1 Continuous Gas Concentration Cells

An electrochemical heat engine based on iodine vapor being expanded through an isothermal electrolyte [$PbI_2(\ell)$], capable of dissociating the working fluid into ions, has been developed. Nickel and platinum electrodes were employed. Regeneration was accomplished by cooling the original hot end and vaporizing the iodine from the original cold end. The cell voltage reversed accordingly. The internal resistance of these cells was very high. Advanced cell designs were tested. The OCV of the cell with enough I_2 to give 1 atm of I_2 vapor at T_2 was 0.17 V (R_i = 2.9 ohms). With a 24.5-ohm load, 6.2 mA were drained from the cell. However, as the cell was operated, its internal resistance increased continuously. Laboratory cells also were operated with the system $Hg(g)|Hg_2Cl_2|Hg(g)$, with tungsten or platinum electrodes. The system $Na(g)|NaCl(\ell)|Na(g)$ and the corresponding potassium cell also were considered as possible candidates for cells of this type. The alkali-metal-based systems were found to display a much more favorable OCV than I_2 or Hg systems. The major difficulty associated with this type of cell is the need to maintain the liquid electrolyte integrity when it is subject to a pressure gradient.

IV.1.2 The Sodium Heat Engine

The Ford Motor Company's sodium heat engine is similar to the cells described in Sec. IV.1.1 but does not have the problems associated with a liquid electrolyte subjected to a pressure difference. The elegant solution to this problem was to use as the sodium ion conductor, the solid electrolyte β"-alumina, which separated the high and low pressure zones, in a closed-cycle device in which fluid sodium circulated. The schematic diagram of this electrochemical heat engine is shown in Fig. S-7. In the high temperature (T_H) area of the device, fluid sodium is at pressure P_H (upper region), which is higher than the pressure in the lower region, P_L. The liquid sodium is heated to T_H and sodium is oxidized to sodium ions and electrons, which leave the high pressure zone via the negative electrode to the external load. The sodium ions produced migrate through the solid electrolyte as a result of the pressure difference ($P_H - P_L$) across the electrolyte. At the low pressure side of the solid electrolyte, a suitable inert porous electrode (the cathode) coats the electrolyte. Sodium ions traverse the solid electrolyte and are reduced at the porous electrode by the electrons that left the high pressure zone, thus forming sodium metal. Neutral sodium evaporates from the porous electrode at pressure P_L and temperature T_H, passing in the gas phase to a condenser at T_L ($T_L < T_H$). Condensed liquid sodium is returned to the high pressure side by means of an electromagnetic pump (thus completing the cycle) without the movement of mechanical parts--only circulation of fluid sodium. The work output is only electrical, equivalent to that of the isothermal expansion of sodium from P_H to P_L at T_H. A theoretical analysis of the efficiencies of these devices under no load and under load, neglecting parasitic heat losses, has been performed. Expressions for several sources of polarization as well as for the thermoelectric effect across the electrolyte have been derived.

Initial performance (1975) was 0.2 W/cm^2, with an overall efficiency of ~10% and short lifetimes (1 week) due to the decay of the ceramic material. This performance improved to ~0.7 W/cm^2 with an overall efficiency of ~20%, the performance being limited mostly by interfacial polarization. It appears that power outputs of 1 W/cm^2 are feasible in this system. With such efficiencies these devices are very light (~30 kW/100 lb) compared with turbines (30 kW/750-1000 lb).

IV.2 MULTIPLE CELLS

The electrochemical heat engines described in this section are composed of at least two closed cells that operate at the same temperature and are connected in electrical opposition (see Type 5 and Fig. S-5). The electrochemical reactions involve one gaseous reactant. The engine produces external work on a load when, by some mechanical means (e.g., by cooling one trap or one cold finger associated with the cells), the equilibrium partial pressure of this gaseous reactant is different in both cells. This difference in partial pressure will drive the reaction of the gaseous substance and will have minimal effect on the condensed phases of the electrochemical cells. The net driving force of the cycle is independent of any property of the electrolyte at open circuit. If the electrode kinetics are fast, little polarization should be observed under current drain. These systems run in cycles. After discharge of one cell and consequent charge of the other, with the consequent performance of electrical work on the external circuit, it is necessary to cool down the trap (or cold finger) that originally was hot and to heat the trap originally cold, thus reversing the role of the electrochemical cells. In principle one can conceive of this type of regeneration being applicable whenever the activity of a chemical substance in one of the cells can be made different from its activity in the other cell. In fact, the type of regeneration performed in these cells is a particular case of electrothermal regeneration. The maximum efficiency possible for these engines is the Carnot efficiency.

These cells were first reported by Lockheed and referred to as regeneration by an electrolysis at low pressure. The systems envisioned for this type of regeneration were $Pb|PbI_2|I_2$ or $Cd|CdI_2|I_2$. The partial pressures of iodine vapor are kept different by the different temperatures in cold traps--one at T_L and the other at T_H, the temperature of the cells. Iodine is at low equilibrium partial pressure at T_L, and therefore at one side of the cell iodine vapor discharges. The condensed iodine is transferred via a nonreturn valve to the hot trap at T_H, where it vaporizes and is ionized at the electrode. Therefore, the system might be run in cycles, with one trap being first cold, thus condensing I_2, and then heated so that the cell is reversed. Electrolysis of CdI_2 at 550°C into a liquid nitrogen trap for the iodine gave currents up to 2 A/cm^2 with a coarse-pore carbon electrode. However, the coulombic efficiency was low due to the high solubility of cadmium in molten cadmium iodide (30%-40%). The major limitations for a high thermodynamic efficiency are the need for a high T_H but not too high an equilibrium pressure (to avoid sealing problems). Kinetic problems at the gas electrode are liable to limit this type of cell, as well as differences in current efficiencies between the two electrochemical cells. The major limitation of this type of cell with iodine or diatomic gases is the low voltage obtained per cell; stacking of several series-connected cells will be necessary to obtain practical voltages.

At Los Alamos Scientific Laboratory another cell configuration of this type has been proposed. Studies were made of the systems $Ag|\alpha\text{-}AgI|I_2$; $Ag|AgI\text{-}KI$(molten eutectic)$|I_2$; and Li|molten alkali metal iodides$|I_2$. The $Ag|I_2$ cell with the solid electrolyte α-AgI showed polarization even at small current drain. The $Li|I_2$ cell was also tested in laboratory cells. These cells are reported to have constant internal resistances of 0.3 ohm cm^2 to 0.8 ohm cm^2, from 0.25 A/cm^2 (discharge) to 0.80 A/cm^2 (charge), with T_H = 350°C and T_L = 25°C. The net voltage obtained at open circuit is 0.29 V and, assuming that polarization effects are small, 0.23 V could be obtained at 0.1 A/cm^2.

Applications projected for these heat engines couple power generation with a chemical storage system, which is one of the unique advantages of these systems over those reported in Sec. IV.1. See Table S-1 for a summary of the performance of these cells compared to those in Sec. IV.1.

IV.3 SUMMARY AND DISCUSSION OF TRES TYPES 5 AND 7

Table S-1 shows that the sodium heat engine (Type 7 engine) is the TRES of highest power demonstrated to date. In fact, this is a very interesting approach to TRES with no need for chemical regeneration steps but with a major limiting requirement--a proper solid electrolyte that is a stable superionic conductor at the desired temperature range. Most of the good solid electrolytes operate at elevated temperatures. For this reason, research of solid electrolytes for operation at lower temperatures should be strongly encouraged.

The electrolysis at reduced pressures (Type 5) has mass transfer problems. Very low power outputs have been obtained with the systems attempted to date.

SECTION V

COUPLED THERMAL AND ELECTROLYTIC REGENERATION - GENERAL

In the electrothermal regeneration mode, the electrochemical reaction products (see Type 4 and Fig. S-4) are regenerated by electrolysis at a temperature $T_2 \neq T_1$. The cells are connected to oppose each other electrically (back to back). The operation of the energy converter is made continuous by sending CA (the electrolyte) formed in the galvanic cell reaction at T_1 to the electrolyzer at T_2, where the galvanic cell reactions drive the electrolysis of CA into C and A. These reactants are returned to the galvanic cell at T_1, completing the closed-cycle operation.

If $T_1 = T_2$, an operation similar to that of a secondary rechargeable battery is achieved with only electrolytic regeneration taking place and with a net OCV of zero. If $T_1 \neq T_2$, electrothermal regeneration is operative. The basic requirement is that the cell voltage of T_2 be <u>less</u> than that at temperature T_1 ($V_2 < V_1$). Thus, the cell voltage at T_1 is used in part to perform the regeneration of the original reactants of cell 1 at T_2, and the remaining voltage is used to perform useful electrical work in the external load. If $T_2 > T_1$, the electrothermal regeneration is being performed by electrolysis at a higher temperature than that of the galvanic cell; the free energy of formation of CA is less negative with increased temperature. If $T_2 < T_1$, the regeneration is performed by electrolysis at a lower temperature. The sign of $(dE/dT)_P$ determines the type of regeneration. Examples in which $T_2 > T_1$ are more common in the literature.

Another important requirement for this type of regeneration is that the electrode reactions $C \rightleftarrows C^+ + e^-$ and $A + e^- \rightleftarrows A^-$ be capable of sustaining high current densities (high exchange currents, low activation overpotentials, low electrode polarization effects in general, and low internal cell resistance) and that they present high coulombic efficiencies, i.e., the same characteristics as for a secondary battery.

There is a temperature at which regeneration starts to take place spontaneously $[\Delta G(T_x) = 0]$, with no need for electrolysis (at higher or lower temperatures). There are few practical examples of systems of this type.

In principle, another possibility for operating electrothermally regenerative systems without transferring reactants and products from one cell to the other (as shown in Fig. S-4) is to reverse the operating temperatures of the two cells. Thus, after the electrolysis at T_2 is completed with the discharge of the cell at T_1 (and concomitant electrical work produced in the external load), one can envision heating cell 1 up to T_2 and cooling down cell 2 to T_1, reversing the roles of the two cells, and obtaining work on the electrical load periodically.

The efficiency of the electrothermally regenerative system is also Carnot limited, as is thermal regeneration. Compared to thermal regeneration, the electrothermal regeneration mode presents the advantage of an inherently simple separation of reactants. For the systems in which there is a flow of reactants and products, the complexity of the device design is similar to that encountered for solely thermal regeneration. Disadvantages of the electrothermal regeneration are polarization at the electrodes in the electrolyzer and possible materials problems at the higher temperatures. These disadvantages have parallels in thermal regeneration in the slow rates of thermal decomposition and materials problems of the regenerator.

V.1 HIGH TEMPERATURE ELECTROLYSIS

V.1.1 Molten Salt Media

In the late fifties, two groups independently pursued the electrothermal regeneration method applied to metal|metal halides|halogen systems as described in Fig. S-4. The cold galvanic cell reaction product flows to the high temperature electrolyzer(s), where the reactants of the cold galvanic cell are regenerated electrolytically, cooled down, and transferred back to the cold galvanic cell. The system $Na(\ell)|$molten $NaCl|Cl_2$ was studied at the Delco-Remy Division of GMC. At Lockheed, research on the electrothermal regeneration mode was applied to the systems $Pb|PbI_2|I_2$, $Cd|CdI_2|I_2$, and $Li|LiI|I_2$ as a continuation of the previous efforts on regenerative systems.

At the Delco-Remy Division, the choice of systems was based on electrolytes that exhibited a wide liquidus range; the product of the galvanic cell reaction was the electrolyte. The $Na|NaCl|Cl_2$ system (NaCl: mp 801°C; bp ~1450°C) conforms to most of these criteria. The cell exhibited a high OCV--3.24 V at 827°C--which decreased with the increase in temperature to 3.14 V at the sodium melting point (880°C) and 2.55 V at 1220°C--a difference in OCV of 0.7 V for a 390°C temperature difference. These cells were studied on charge and on discharge in the 827°-1057°C range and showed the ability to be charged and discharged at high current densities (e.g., at 827°C discharge currents above 3500 mA/cm^2, with ohmic polarization only up to 4300 mA/cm^2). The ability of these cells to undergo charge (electrolyzer reaction) and discharge (galvanic cell reaction) over a wide temperature range was taken as a partial feasibility demonstration of the concept of electrothermal regeneration. No complete coupling of the galvanic cell and electrolyzer, with the appropriate flow of materials, was tested. Sodium dissolution in the molten sodium chloride at that temperature decreased the coulombic efficiency of the system.

For the $Li|LiI|I_2$ system at 500°C, the OCV was 2.5 V (close to the theoretical value). The current-voltage curves showed that current densities of 320 mA/cm^2 could be obtained at 1.5 V. About 2 mol % of lithium dissolved in the lithium iodide at this temperature, thus decreasing the coulombic efficiency. The electrolyses of CdI_2 (450°C) and PbI_2 (815°C) showed only ohmic polarization. In continuous operation, heat exchanger inefficiencies lead to irreversible losses. However, these systems have inherent easy separation of reactants and products. Since the galvanic cell is a battery, energy storage can be achieved in these systems. The batteries can be operated temporarily for power generation, in addition to operation as energy converters. The theoretical operational efficiencies are generally higher than the corresponding efficiencies for conventional thermoelectric devices (or thermogalvanic cells), in which the electric and thermal conduction paths cannot be separated. Most problems common to electrochemical devices utilizing gas electrodes (plugging or flooding of the electrodes) obviously would be encountered here. Finally, because the electrolyzers have current efficiencies lower than the galvanic cells, one can envision the need for more than one electrolysis cell coupled with each galvanic cell to achieve practical regeneration rates.

V.1.2 Aqueous Media

An example of a potential electrothermally regenerative system has been described recently and is based on the half-reactions:

$$\begin{array}{lcl}
Cu(NH_3)_4^{2+} + e^- & \rightleftarrows & Cu(NH_3)_2^+ + 2\ NH_3 \\
Fe(CN)_6^{4-} & \rightleftarrows & Fe(CN)_6^{3-} + e^- \\
\hline
Cu(NH_3)_4^{2+} + Fe(CN)_6^{4-} & = & Cu(NH_3)_2^+ + Fe(CN)_6^{3-} + 2\ NH_3
\end{array}$$

These reactions were selected because of their large molar entropy changes. The two half-reactions must be separated by semipermeable membranes. Power output densities for these cells were calculated assuming ohmic polarization only, and the authors claim that 6.4 W/m^2 are feasible for operation between 30° and 90°C. No estimate was made of internal cell resistance variation with time or pumping and heat exchanger requirements. Efficiencies of 8% were claimed (half of the Carnot limit). The efficiency of other systems was analyzed theoretically. The authors propose to couple this type of energy converter with flat-plate solar collectors for home use in cogeneration.

V.1.3 Hydrogen-Oxygen Fuel Cell Coupled with High Temperature Water Electrolysis

The combination of fuel cells operating with hydrogen and oxygen at low temperature, producing water which could be electrolyzed at a high temperature (>1000°C), has been proposed, and thermodynamic calculations have been performed. Electrolysis of water at >1000°C has received research emphasis in the context of possible coupling with fusion reactor heat. From current technology data for high temperature electrolysis, this coupling does not appear feasible at the moment.

V.2 FLUORIDES OF URANIUM(VI) OR CERIUM(IV) AND ARSENIUM(III) - SPONTANEOUS CHARGE REACTION

Two examples have been reported of galvanic cells that can be recharged by high temperature electrolysis or, if the temperature is high enough, by the reverse galvanic cell. The reverse cell also acts as a power generator and regenerates the original reactants of the low temperature galvanic cell; therefore, the cell operates at one polarity at low temperature and at the opposite polarity at higher temperature. The high temperature cell regenerates the cell to its original electrochemical state. These cells are based on the redox couple AsF_3/AsF_5, for which the relative stability of the two fluorides rapidly changes with increased temperature.

V.3 THERMOCELL REGENERATORS

A combination of a galvanic cell in molten salt media and a thermocell has been described (Types 4 and 6). The electrodes of the thermocell are short-circuited for the regeneration of the reactants for the galvanic cell, provided that the thermocell voltages developed are higher than the decomposition voltage of the salt. The decomposition products are continuously removed from the thermocell and returned to the galvanic cell. This combination was called a regenerative, molten salt, thermoelectric fuel cell. Laboratory cells were built, one with $ZnCl_2$ and another with $SnCl_2$.

V.4 DISCUSSION OF TRES TYPE 4

Although the coupling of thermal and electrolytic regeneration was suggested in 1958, very few systems have been attempted. The very high temperature systems that were tried exhibited materials problems and low coulombic efficiencies. The systems described in Sec. II and some of Sec. I can conceivably operate in this regeneration mode. This type of regeneration has been explored to a lesser extent than thermal or electrolytic regeneration alone, but it can perhaps broaden the nature of the systems to be investigated. Media operating at lower temperatures should be investigated.

SECTION VI

CONCLUSIONS AND RECOMMENDATIONS

Most of the technical activities described in this review were either performed or originated many years ago and, most importantly, with specific applied objectives. Most of the work was aimed at the use of nuclear heat sources, and much of it had as its ultimate goal the development of space power systems, for which weight and zero gravitational operation were vital considerations.

It appears to us that as a result of significant time constraints imposed by the proposed space utilization timetable, much of the work involved certain preliminary experiments followed by a perhaps premature selection of a particular system for development. In certain instances, devices were fabricated and tested prior to the availability of basic chemical and/or electrochemical system information. In some cases (e.g., the thermogalvanic cells described in Sec. III), primarily scientific information was sought. In some instances, albeit far fewer (we felt), devices were fabricated based upon a known and determined scientific base.

It is worth pointing out that the reactor heat source utilization, which was one of the driving forces behind much of this work, was based on regeneration at a high temperature--usually 800°C or higher. Desire for high current efficiency tended to result in a system capable of operating over a several-hundred-degree temperature gradient. Systems operating at much lower temperatures have not been thoroughly investigated but may well be relevant to matching with solar heat sources. Our recommendations do not constitute an official position on the part of the Solar Energy Research Institute. These recommendations are intended to suggest areas for which research in either science or engineering would have long-range benefit to a TRES program. They are not intended as indications of proposed or intended development programs of a specific nature. In making these recommendations, we have not engaged in engineering or system evaluation of particular concepts and, in fact, have purposely avoided doing so. Our recommendations attempt to assess whether past research may be worthy of renewed investigation because of the availability of new information or tools and techniques and because of the very significant changes in perspective posed by a terrestrial, solar heat source. We hope the report and subsequent evaluation of both it and our recommendations will result in new consideration of the science involved in TRES systems.

For terrestrial applications using solar heat sources, some general recommendations concerning thermally regenerative electrochemical systems can be made:

- Systems operating at lower temperatures should be investigated more thoroughly.
- The search for possible new types of TRES should be continued. Most of the obvious candidate systems for TRES have been tried; however, the development of new concepts is possible.

Our recommendations of areas of research to pursue that are related to TRES are very broad generalizations (as opposed to specific system decisions). Our assessment of the work reported and evaluated in this document convinces us this is the most reasonable approach, given the constraints discussed above.

- Molten Salt Chemistry and Electrochemistry
  A broad view of the TRES area indicates the significant attempts to employ a wide variety of molten salt systems. Research in this area is rather limited at this time in the United States. New classes of molten salts have been developed in the past years, but detailed understanding of these systems is lacking. Pertinent questions have not been addressed, such as "Are electrode processes intrinsically fast at elevated temperatures, simply by virtue of the higher temperature?" Recent developments involving considerations of transport and structure in molten salts suggest that important, germane scientific information now exists (or can be obtained) that may not have been known or recognized when much of the work reported here was performed. While a good deal of the work reported here had a research component, the major thrust of most of it was developmental. Hence, additional understanding of molten salt systems--and we might well include even concentrated electrolytes and hydrate melts--is important to this area. Structural, transport, electrochemical, and general physical properties, including valid thermodynamic data, are areas where research would be applicabile to TRES development.

- Solid-State Chemistry
  In a number of instances one can observe the need for either new materials (particularly stable, superionic conductors) or a better understanding of existing materials, such as stabilized zirconia or beta-alumina. Research efforts in these areas are very limited, particularly with regard to high temperature materials, except for oxide transport. In a number of cases, materials employed as ionic conductors in work reported here were used because they existed and were readily available, not because they were optimal. Kinetics and mechanisms of electrochemical reactions taking place at the solid electrolyte/electroactive material/current collector interface also constitute an area of interest. The recent development of a large number of surface spectroscopic techniques provides tools that would result in new understanding.

  As a subset of this area, it appears that gas permeation through metals could be studied, again making use of recently developed surface techniques to obtain basic information of benefit to an embryonic TRES program.

- Materials Science
  A quick glance through the body of this report makes obvious the materials problems--containment, bonding, corrosion--that plagued numerous activities; and, obviously, the higher the temperature, the greater the problem. A broad program in supporting materials research is recommended.

- Aqueous Systems and Electrochemistry under Extreme Conditions
  While the properties of aqueous systems at room temperature are well studied, activities related to TRES suggest that one may seek to employ aqueous electrolyte systems at unusually high temperatures and pressures. Chemical and electrochemical research in aqueous systems at much over 100°C is not a well-studied area, but it is one which would be of broad interest to this and other solar programs.

- Electrochemical Engineering
  The development of any low voltage source--and all TRES are inherently low voltage--ultimately would require electrochemical engineering support in such areas as transport and battery formation. Electrochemical engineering does not appear to have paid much attention to the high temperature area except for certain specific process work, and general consideration of this problem area would be most useful. It is our opinion that such input is required for useful systems analysis.

- System Analysis
  To our knowledge, no integral system analysis has been performed to assess the practicality of a complete TRES. In fact, such an analysis may not be possible at this time, based on available literature data. For example, it is not clear whether sufficient and significant polarization data for cells can be found. Nevertheless, it may be worth considering this approach for one or more of the systems reviewed, keeping firmly in mind that no electrochemical system (i.e., series arrangement of cells) has been investigated and even cell data is meager in most cases. We are unable to address the ultimate use of a TRES (i.e., central- or dispersed-power application), but clearly this consideration is important to an integral system analysis.

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SECTION VII

REFERENCES

1. Liebhafsky, H. A. "Regenerative Electrochemical Systems: An Introduction." Regenerative Emf Cells. C. E. Crouthamel and H. L. Recht, eds. Advances in Chemistry Series. Vol. 64. Washington, DC: American Chemical Society; 1967; pp. 1-100.

2. Examples of redox regenerative systems: (a) Redox Flow Cell Development and Demonstration Project - Calendar Year 1977. Report No. NASA TM-79067. Prepared under Interagency agreement E(49-28)-1002. 1979. (b) Ciprios, G.; Erskine, W.; Grimes, P. G. "Redox Bulk Energy Storage System Study. Vols. 1 and 2. Final Reports N 77-33608 and N 77-33609. 1967. (c) Asimura, S.; Miyaki, Y. "Redox-Type Fuel Cell. VII. Polarization Characteristics of the Redox-Type Fuel Cell Anode at Flow-Through Porous Carbon Electrodes." Denki Kaguku. Vol. 40: pp. 50-54; 1972.

3. Austin, L. G. Fuel Cells: A Review of Government Sponsored Research, 1950-1964. NASA-SP-120. pp. 153-203.

4. Kerr, R. L. "Regenerative Fuel Cells. Proc. of the 29th Performance Forecast Selected Static Energy Conversion Devices Meeting. AGARD, Propulsion and Energetics Panel; 1967; Liege, Belgium. G. W. Sherman and L. Devol, eds. 1968. pp. 658-711.

5. Regenerative Emf Cells. C. E. Crouthamel and H. L. Recht, eds. Advances in Chemistry Series. Vol. 64. Washington, DC: American Chemical Society; 1967.

6. Examples of electrolytically regenerative systems: (a) McBreen, J.; Yeo, R. S.; Beaufrere, A.; Srinivasan, S. "Hydrogen-Chlorine Energy Storage System." Report BNL-23 670. 1977. (b) Swette, L.; Holleck, G. L. "Hydrogen-Nickel Regenerative Fuel Cell." Final Report No. 339. Contract F33615-73-C-2057. 1974. (c) Wilner, B. M.; Frank, H. A.; Findl, E.; Klein, M. "Electrolytically Regenerative Hydrogen-Oxygen Fuel Cells." U.S. Patent 3,507,704. 1970.

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15. Supplementary Notes

16. Abstract (Limit: 200 words)

Thermally regenerative electrochemical systems (TRES) are closed systems that convert heat into electricity in an electrochemical heat engine that is Carnot cycle limited in efficiency. Past and present work on such systems is reviewed. Two broad classes of TRES are based on the types of energy inputs required for regeneration: thermal alone and coupled thermal and electrolytic. The thermal regeneration alone encompasses electrochemical systems (galvanic or fuel cells) in which one or more products are formed. The regeneration can be performed in single or multiple steps. The compounds include metal hydrides, halides, oxides, chalcogenides, and alloys or bimetallic systems. The coupled thermal and electrolytic regeneration encompasses electrochemical systems (galvanic or fuel cells) regenerated by electrolysis at a different temperature or different pressure. Examples include metal halides and water. Thermogalvanic or nonisothermal cells are included in this category. Also included are electrochemical engines in which the working electroactive fluid is isothermally expanded through an electrolyte. TRES cover temperature ranges from about 20°C to 1000°C. Engines with power outputs of 0.1 mW/cm^2 to 1 W/cm^2 have been demonstrated. Recommendations are made of areas of research in science and engineering that would have long-range benefit to a TRES program.

17. Document Analysis

a. Descriptors Thermal Regeneration; Electrochemical Cells; Regenerative Fuel Cells; Fuel Cells; Thermogalvanic Cells; Thermal Reactors; Distillation; Electrochemical Engines; Electrochemical Heat Engines; Hydrides; Halides; Chalcogenides; Oxides; Bimetallic Systems; Alloy Systems; Electrothermal Systems; Coupled Electrolytic Thermal Regeneration; Double Thermogalvanic System

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