INVESTIGATION OF NEW CATHODE-ANODE COUPLES FOR SECONDARY BATTERIES USING MOLten SALT ELECTROLYTES

TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-63-115
January 1963

DIRECTORATE OF AEROMECHANICS
AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

PROJECT NO. 8173, TASK NO. 817304

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BY RADIO CORPORATION OF AMERICA
SEMICONDUCTOR AND MATERIALS DIVISION
SOMERVILLE, NEW JERSEY)

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E.F. Uhler, G. Stockdale, P. Ritterman, and Dr. G.S. Losier, Authors).
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FOREWORD

This final report on the evaluation of new cathode-anode couples for secondary batteries was prepared by the Radio Corporation of America, Semiconductor and Materials Division, Somerville, New Jersey. The program is sponsored by the Flight Accessories Laboratory of the Flight Vehicle Power Branch, Aeronautical Systems Division, Air Force Systems Command, United States Air Force. Wayne S. Bishop and James E. Cooper were the project engineers for the Flight Accessories Laboratory.

This report covers investigations carried out under U.S. Air Force Contract AF-33(657)-7758, and includes the period from November 1961 to November 1962.
ABSTRACT

A final report is presented covering an investigation of the most direct and systematic approach in selecting the most promising materials for the development of higher capacity secondary batteries for space applications.

The experimental approach, materials, and necessary precautions required in molten-salt technology are summarized. Advantages and disadvantages of the various molten salt electrolytes considered are presented.

Experimental procedures and couple materials investigated are discussed. The experimental results for the molten-salt cells investigated are presented. Data are presented for cells with fluoride, chloride and sulfate molten-salt electrolytes.

Objectives and results of a ceramic separator study phase of the program are included. The design of a molten-salt secondary battery which was constructed during the course of the program is described, along with fabrication procedures of this battery. Theoretical calculation for the initial heat input versus heat output and the heat loss due to cell radiation is presented. Recommendation for future work and conclusions in both areas are given.

The publication of this report does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.
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1. INTRODUCTION

The development of secondary batteries with higher capacities than those currently used for space applications required a re-evaluation of the active materials.

The objective of this program was to provide design criteria for the development of long-life, light-weight secondary batteries through the investigation of new anode-cathode couples and their associated electrolytes and separators. For the selection of new anode-cathode couples, it was established that the theoretical energy-to-weight ratio of the reactant material, based on their free energy release at 25°C, should not be less than 500 watt-hours per pound.

The most direct and systematic approach to the selection of the most promising materials was through the consideration of the ampere-hour-per-pound capacity and theoretical half-cell potential of the possible anode and cathode materials. Data for the pounds of material required to supply 500 ampere-hours and theoretical reversible potential in an aqueous electrolyte system of some representative cathode materials are given in Table I, and similar data for some representative anode materials are given in Table II. The theoretical capacity (C) in watt-hours per pound of various couples can be calculated from the data in Tables I and II by the following equation:

\[
C = \frac{(E_A - E_C)}{500 (lb_a + lb_c)}
\]  \hspace{1cm} (1)

where \( E_A \) is the reversible emf of the anode, \( E_C \) is the reversible emf of the cathode, \( lb_a \) is the weight in pounds of anode material required to supply 500 ampere-hours of electrical energy, and \( lb_c \) is the weight in pounds of cathode material required to supply 500 ampere-hours of electrical energy.

This equation shows that the desirable materials should have a high ampere-hour-per-pound capacity and that, if one of the reactant materials does not have a high capacity, \( E_A - E_C \) must be large. The ratio within the brackets must also be greater than 1 for a particular couple to have a theoretical capacity greater than 500 watt-hours per pound.

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# TABLE I. THEORETICAL PROPERTIES OF SOME CATHODE MATERIALS INVESTIGATED UNDER THIS PROGRAM.

<table>
<thead>
<tr>
<th>CATHODE MATERIAL</th>
<th>lb&lt;sub&gt;c&lt;/sub&gt; (per 500 amp-hour)</th>
<th>E&lt;sub&gt;A&lt;/sub&gt; (emf)</th>
<th>E&lt;sub&gt;A&lt;/sub&gt; (emf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>0.33</td>
<td>-1.23</td>
<td>-0.401</td>
</tr>
<tr>
<td>m-Dinitrobenzene</td>
<td>0.59</td>
<td>-0.87</td>
<td>0.48</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.66</td>
<td>-0.141</td>
<td>0.66</td>
</tr>
<tr>
<td>Fluorine</td>
<td>0.78</td>
<td>-2.87</td>
<td>2.87</td>
</tr>
<tr>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt; → Cu&lt;sup&gt;0&lt;/sup&gt;</td>
<td>1.3</td>
<td>-0.34</td>
<td>-</td>
</tr>
<tr>
<td>Chlorine</td>
<td>1.46</td>
<td>-1.37</td>
<td>-1.37</td>
</tr>
<tr>
<td>Cupric Oxide</td>
<td>1.65</td>
<td>-</td>
<td>0.22</td>
</tr>
<tr>
<td>Manganese Dioxide (2e)</td>
<td>1.77</td>
<td>-1.28</td>
<td>-</td>
</tr>
<tr>
<td>Pd&lt;sup&gt;2+&lt;/sup&gt; → Pd&lt;sup&gt;0&lt;/sup&gt;</td>
<td>2.20</td>
<td>-0.83</td>
<td>-</td>
</tr>
<tr>
<td>Ag&lt;sup&gt;2+&lt;/sup&gt; → Ag&lt;sup&gt;0&lt;/sup&gt;</td>
<td>2.23</td>
<td>-0.79</td>
<td>-</td>
</tr>
<tr>
<td>Silver II Oxide</td>
<td>2.54</td>
<td>-</td>
<td>-0.57</td>
</tr>
<tr>
<td>Silver Chloride</td>
<td>5.94</td>
<td>0.222</td>
<td>-</td>
</tr>
<tr>
<td>Cuprous Chloride</td>
<td>4.97</td>
<td>-0.522</td>
<td>-</td>
</tr>
<tr>
<td>Nickel Chloride</td>
<td>2.68</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nickel Oxide</td>
<td>1.54</td>
<td>-</td>
<td>0.5 (approx)</td>
</tr>
</tbody>
</table>

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### TABLE II. THEORETICAL PROPERTIES OF THE ANODE MATERIAL INVESTIGATED UNDER THIS PROGRAM.

<table>
<thead>
<tr>
<th>ANODE MATERIAL</th>
<th>1b a POUNDS (per 500 amp-hr)</th>
<th>E_A (emf)</th>
<th>E_B (emf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.0415</td>
<td>0.0</td>
<td>0.83</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>0.085 - 0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Borohydrides</td>
<td>0.11 - 0.12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Beryllium</td>
<td>0.185</td>
<td>1.7</td>
<td>2.3</td>
</tr>
<tr>
<td>Lithium</td>
<td>0.285</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.37</td>
<td>1.67</td>
<td>2.35</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.49</td>
<td>0.95</td>
<td>-</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.50</td>
<td>2.34</td>
<td>2.67</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.71</td>
<td>0.71</td>
<td>1.2</td>
</tr>
<tr>
<td>Iron</td>
<td>1.14</td>
<td>0.44</td>
<td>0.87</td>
</tr>
<tr>
<td>Manganese</td>
<td>1.14</td>
<td>1.05</td>
<td>1.47</td>
</tr>
<tr>
<td>Zinc</td>
<td>1.34</td>
<td>0.76</td>
<td>1.22</td>
</tr>
<tr>
<td>Cadmium</td>
<td>2.31</td>
<td>0.402</td>
<td>0.815</td>
</tr>
<tr>
<td>Lead</td>
<td>4.26</td>
<td>0.126</td>
<td>0.578</td>
</tr>
</tbody>
</table>
It is recognized that many of the potentials, in particular those in Table II, are values calculated from other thermodynamic data, and are not attainable in aqueous electrolytes. The variation of the theoretical potential does not vary enough to change general conclusions on the classes of available anode and cathode materials listed below. This is particularly true of the anodes, which determine the selection of electrolyte systems. A detailed listing of theoretical capacities is not given because such a listing would require a critical evaluation of the sources of information, such as the free energy of ions and standard states in these solvents.

For ease of discussion, the available cathode materials may be grouped into four general classes:

a. low-molecular-weight elements, e.g., F₂, Cl₂, O₂, H₂, and S.

b. inorganic compounds with a high available-oxygen content, e.g., OsO₄, CuO, AgO, NiO₂, and MnO₂ (2-electron change).

c. metal-metal ion electrodes
   \[ \text{Cu}^{++} \rightarrow \text{Cu}, \quad \text{Ag}^{+} \rightarrow \text{Ag}, \quad \text{Rh}^{++} \rightarrow \text{Rh}, \quad \text{Sb}^{+++} \rightarrow \text{Sb} \]

d. organic materials, e.g., quinone, nitroguanidine.

The available anode materials on the basis of their ampere-hour capacity and theoretical emf in aqueous electrolytes may be classed as follows:

a. the low-molecular-weight metals in Group 1A, IIA, and Al.

b. hydrogen.

c. metals in the fourth row of the periodic chart in Groups VI, VII, and VIII.

d. boron and its hydrides.

e. carbon and its derivatives.
2. SUMMARY

The reversibility of various anode-cathode combinations using a molten-salt electrolyte has been demonstrated. Magnesium has been shown to be the most desirable anode material when coupled with any of a variety of oxide and chloride cathode materials. A molten-chloride electrolyte was found to be most desirable because it eliminated numerous problems with respect to containment, high temperature, and chemical complexing problems which were encountered when molten fluorides and sulfate electrolytes were used.

A ceramic body (10% Na$_2$O) has been developed which permits single-ion mobility of sodium ion, thereby permitting it to be used as a stable separator in a molten-salt secondary battery. Other ceramics capable of permitting ion mobility of ions other than sodium (e.g., lithium, oxygen) have been investigated.

A molten-salt secondary battery has been constructed. This 2.6-volt battery was capable of a 20-ampere discharge for 35 minutes. The relationship of heat input to heat output and the heat loss due to cell radiation of this battery have been calculated.
3. TECHNICAL DISCUSSION

3.1 GENERAL

The main objective of this program was to provide design criteria for long-life, light-weight secondary batteries through the investigation of new cathode-anode couples and their associated electrolytes and separators. To this end, a magnesium/nickel chloride/nickel molten-salt secondary battery of 2.60 volts was fabricated to demonstrate the feasibility of the system for aerospace applications. In this report, the method of construction and electrochemical calculations of this battery are presented along with recommendations for future work.

3.2 EXPERIMENTAL APPROACH

The experimental studies of molten-salt systems were conducted to determine the reversibility of various anode-cathode couples under charge and discharge conditions. Combinations of known reversible anode and cathode materials were used in the cells studied. Because of the various anode and cathode materials to be evaluated, many possible combinations of electrodes existed. In each group, the anode-cathode combinations used ceramic separators. The groups were divided as follows:

<table>
<thead>
<tr>
<th>Group</th>
<th>Anode/Separator/Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>a.</td>
<td>( M_a )/ceramic/( M_a \text{Cl} ), ( M_c \text{Cl}/M_c )</td>
</tr>
<tr>
<td>b.</td>
<td>( M_b )/( M_b \text{Cl} ), NaCl/ceramic/NaCl , ( M_c \text{Cl}/M_c )</td>
</tr>
<tr>
<td>c.</td>
<td>( M_b )/( M_b \text{Cl} ), NaCl/ceramic/( M_a ), ( M_c \text{Cl}/M_c )</td>
</tr>
</tbody>
</table>

where:

\( M_a \) = Anode material having a cation which is mobile in the ceramic separator.

\( M_b \) = Anode material having a cation which is not mobile in the ceramic separator.
Various metal-metal-ion cathodes.

Various metal-sulfate electrolytes.

Various metal-oxide cathodes which function reversibly as electrodes of the second kind.

The couples chosen for experimental purposes were selected on the basis of:

a. simplicity of the composite system.

b. known reversibility of the components.

c. watt-hour capacity of the reactant materials.

Table III lists the anode-cathode couples selected for evaluation in a molten-salt electrolyte. These couples were selected on the basis of the theoretical capacity of the reactant materials at an operating temperature of 700°C and the known reversibility of the selected electrodes.

3.3 SELECTION OF ANODE ELECTROLYTE AND CATHODE MATERIALS

3.3.1 Anode Materials

Because of their high ampere-hour capacity and theoretical electromotive force, the alkali and alkaline-earth metals and aluminum were shown to be the most desirable anode materials. In addition, these anode materials were selected for use in the program because of their ability to be used with a wide range of metal-metal ion cathodes and various metal-oxide cathodes which function reversibly as anodes of secondary cells.

3.3.2 Electrolytes

Since the anode materials used in the existing program are irreversible in aqueous electrolytes, they must be used with nonaqueous electrolytes. Molten salts were selected as electrolytes because of their relatively high conductivity in comparison with other nonaqueous electrolytes, and because a considerable amount of experimental data has been published which indicates that reversible electrodes are feasible in this type of electrolyte. A comparison of the electrical conductivity and operating temperature range of some of the electrodes considered is shown in Figure 1 and 2. It should be noted that the conductivity and temperature range for molten salts is higher than those of all other systems.
### TABLE III. COUPLES SELECTED FOR EVALUATION WITH A CERAMIC SEPARATOR

<table>
<thead>
<tr>
<th>ANODE</th>
<th>CATHODE</th>
<th>BASE METAL FOR CELL CATHODE</th>
<th>ELECTROLYTE</th>
<th>THEORETICAL EMF AT 700°C (volts)</th>
<th>THEORETICAL CAPACITY OF REACTANT MATERIAL AT 700°C (w-hr/lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>AgCl</td>
<td>Ag(Pt)</td>
<td>LiCl, NaCl</td>
<td>(60, 40 mole-%)</td>
<td>2.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MgCl₂, NaCl, AgCl</td>
<td>(45, 50, 5 mole-%)</td>
<td>257</td>
</tr>
<tr>
<td>Mg</td>
<td>NiCl₂</td>
<td>Ni(Pt)</td>
<td>MgCl₂, NaCl</td>
<td>(48, 52 mole-%)</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MgCl₂, NaCl, NiCl₂</td>
<td>(45, 50, 5 mole-%)</td>
<td>339</td>
</tr>
<tr>
<td>Al</td>
<td>NiCl₂</td>
<td>Ni(Pt)</td>
<td>AlF₃, NaF</td>
<td>(60, 40 mole-%)</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MgCl₂, NaCl, NiCl₂</td>
<td>(45, 50, 5 mole-%)</td>
<td>238</td>
</tr>
<tr>
<td>Al</td>
<td>AgCl</td>
<td>Ag(Pt)</td>
<td>AlF₃, NaF</td>
<td>(60, 40 mole-%)</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MgCl₂, NaCl, AgCl</td>
<td>(45, 50, 5 mole-%)</td>
<td>151</td>
</tr>
<tr>
<td>Mg</td>
<td>CuCl</td>
<td>Cu(Pd)</td>
<td>MgCl₂, NaCl</td>
<td>(48, 52 mole-%)</td>
<td>1.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MgCl₂, NaCl</td>
<td>(48, 52 mole-%)</td>
<td>170</td>
</tr>
<tr>
<td>Mg</td>
<td>NiO</td>
<td>Ni</td>
<td>MgCl₂, NaCl</td>
<td>(48, 52 mole-%)</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Li₂SO₄, Na₂SO₄, CaO</td>
<td>(70.6, 28.4, 1.0 mole-%)</td>
<td>340</td>
</tr>
<tr>
<td>Mg</td>
<td>Cu₂O</td>
<td>Cu(Pd)</td>
<td>MgCl₂, NaCl</td>
<td>(48, 52 mole-%)</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Li₂SO₄, Na₂SO₄, CaO</td>
<td>(70.6, 28.4, 1.0 mole-%)</td>
<td>170</td>
</tr>
<tr>
<td>Al</td>
<td>NiO</td>
<td>Ni</td>
<td>AlF₃, NaF</td>
<td>(60, 40 mole-%)</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MgSO₄, Na₂SO₄</td>
<td>(70.6, 29.4 mole-%)</td>
<td>260</td>
</tr>
</tbody>
</table>
FIGURE 1. TYPICAL CONDUCTIVITY RANGES FOR VARIOUS ELECTROLYTES.
FIGURE 2. TYPICAL TEMPERATURE RANGES FOR VARIOUS ELECTROLYTES.
Some of the important generalizations which can be made about molten salts are:

a. Experimental data show that the various anode and cathode materials under consideration are reversible in certain molten salts (ref. 1, 2, 3.)

Electrode reactions in molten salts have been shown to occur at appreciable rates with little polarization at their reversible potential. Pertinent experimental measurements have been made by Flengas (ref. 2), Laitinen (ref. 4, 5) Delimarskii (ref. 6, 7, 8, 9, 10, 11, 14), Piontelli (ref. 12, 13), and Maskovets (ref. 15).

b. Comparison of electrical conductivity of the various classes of electrolytes presented in Figure 1 shows that molten salts are the best electrolytic conductors. The discharge data obtained in thermal cells indicate that polarization of cells with a molten-salt electrolyte will be low. Both factors are favorable to the design of a molten-salt secondary battery.

c. The operating temperature range is over 400°C for molten salts that are stable with respect to reactant materials. There are a few exceptions to this statement. The principle exceptions are molten salts containing aluminum and ammonium ions which would be used with an aluminum anode. The success of couples in molten salts is determined by solution of the containment problems and problems associated with the solubility of the reactants in the molten-salt electrolyte.

A major design problem was the development of an electro-chemically and thermally adequate separator. This is discussed further in this report.

3.3.2.1 Molten-Chloride Electrolytes

A molten-chloride electrolyte has several desirable characteristics, including high stability, high conductivity, and a low-melting point with respect to other molten salts. In addition, more data are available on chloride melts than on any other electrolyte with the possible exception of molten fluorides.

The major disadvantage of a molten-chloride electrolyte is its corrosive nature and its ability to complex some of the desirable anodes and cathodes. However, various studies reported in the literature indicate that molten-chloride electrolytes are suitable with respect to the ionic conductivity required for the present application. In order to eliminate the commonly observed oxychloride formation in a molten-chloride system, precautions which are discussed in this report were taken to use only anhydrous materials.
3.3.2.2 Molten-Sulfate Electrolytes on the Cathode Side

The distinct advantages of a sulfate electrolyte are its lower tendency to complex, and the relative ease with which it may be dried to an anhydrous condition. One disadvantage is the instability of the sulfate ion with some of the reactant anode materials investigated. However, this disadvantage is eliminated when the sulfate electrolyte is used only on the cathode side of the cell and is physically separated from the anode material by the ceramic separator.

3.3.2.3 Molten-Fluoride Electrolyte on the Anode Side

An initial investigation on the use of an aluminum anode involved the use of AlCl$_3$ and NaCl eutectic electrolyte. Because of the vapor pressure and hydroscopic nature of AlCl$_3$, the results obtained in initial tests were erratic. In metallurgical practice, electrolysis of aluminum is made possible by the use of the metal fluoride (AlF$_3$). Therefore, emphasis was placed upon the use of a fluoride electrolyte on the anode side of the experimental cell.

3.3.3 Cathode Materials

The use of a molten-salt electrolyte necessitated the selection of a cathode material from the inorganic oxides that are stable at high temperatures, and which have a high available-oxygen content, such as NiO, or a metal, metal-ion electrode such as AgCl. In the program, the inorganic oxides were investigated more thoroughly because of their high theoretical ampere-hour capacity.

3.3.4 Method of Separation

A basic problem in the selection of secondary couples in systems using molten-salt electrolytes is the separation of the anode and cathode materials. The solubility of the various reversible materials evaluated was an important consideration in this problem of active component separation. Various methods of separation were investigated. A reaction mechanism permitting the reversible mobility of a single ion was selected as the best method of separation. The important phenomenon of the reaction mechanism is the ability of a single ion to be transported reversibly through a ceramic material. The type of ceramic material which was developed during the program permits sodium ion mobility, and also has a higher electrical conductivity and lower operating temperature than other similar materials. Therefore, the coupling of appreciably soluble cathodes to an alkali or alkaline-earth-metal anode was made possible. A reversible
cell based on this principle is illustrated in Figure 3. The electrical conductivity of the ceramic material as a function of temperature is shown in Table IV.

3.3.5 Considerations for Molten-Salt Studies

3.3.5.1 Reactivity of Molten Salts with Oxygen and Water from Air

Because many of the salts under consideration readily hydrolyze, and since the anode materials react with oxygen and water, an inert atmosphere was used.

3.3.5.2 Containers

The containment of molten salts presented many problems because of the temperatures involved and the corrosive nature of many molten salts. Several materials that were found satisfactory as containers are boron nitride, graphite, quartz, pure refractory oxides, and glass. In the experimental studies, boron nitride, quartz, and Pyrex were used.

3.3.5.3 Purity of Materials

In general, investigations of electrode kinetics required that high-purity material be used. This is particularly true of studies for the determination of exchange currents. In the present study, however, the degree of reversibility desired requires a large exchange current and, thus, the effect of impurities was lessened considerably. This does not mean that all reasonable precautions should not be met. Laitinen and his co-workers (ref. 16) have described criteria for electrolyte purity for exchange-current measurements. A particular problem in obtaining high-purity material is the removal of water from the salts without causing hydrolysis. This requires that the salts be dried by special techniques prior to being placed into the cell. The procedure developed by Van Norman and Janz (ref. 17) was used in the present studies and is described in Section 3.4.1.

3.3.5.4 Time to Reach Equilibrium

A general characteristic of molten-salt systems is the time that is required for such systems to reach equilibrium. For example, systems have been reported which did not reach equilibrium for 20 hours (ref 17)
<table>
<thead>
<tr>
<th>ANODE</th>
<th>ELECTROLYTE</th>
<th>SEPARATOR</th>
<th>ELECTROLYTE</th>
<th>CATHODE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-) -Mg</td>
<td>MgCl₂</td>
<td>(Discharge)</td>
<td>Na⁺ Cl⁻</td>
<td>AgCl, Ag⁻ (+)</td>
</tr>
<tr>
<td></td>
<td>NaCl</td>
<td>(Charge)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ceramic</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Discharge:**

\[
\begin{align*}
\text{Mg} & \rightarrow \text{Mg}^{2+} + e^- \\
\text{AgCl} + e^- & \rightarrow \text{Ag} + \text{Cl}^- \\
\text{Mg} + 2\text{AgCl} & \rightarrow \text{MgCl}_2 + 2\text{Ag}
\end{align*}
\]

**Charge:**

\[
\begin{align*}
\text{Mg}^{2+} + e^- & \rightarrow \text{Mg} \\
\text{Ag} + \text{Cl}^- & \rightarrow \text{AgCl} + e^- \\
\text{MgCl}_2 + 2\text{Ag} & \rightarrow \text{Mg} + 2\text{AgCl}
\end{align*}
\]

**FIGURE 3. MECHANISM AND REACTIONS OCCURRING IN A MAGNESIUM/SILVER-CHLORIDE COUPLE WITH A CERAMIC SEPARATOR.**

ASD-TDR-63-115 14
TABLE IV. RESISTIVITY OF A CONDUCTING CERAMIC SEPARATOR
AS A FUNCTION OF TEMPERATURE.

<table>
<thead>
<tr>
<th>RESISTIVITY (Ohm -cm)</th>
<th>TEMPERATURE (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>730</td>
<td>400</td>
</tr>
<tr>
<td>420</td>
<td>450</td>
</tr>
<tr>
<td>140</td>
<td>550</td>
</tr>
<tr>
<td>64</td>
<td>650</td>
</tr>
<tr>
<td>42</td>
<td>700</td>
</tr>
<tr>
<td>25</td>
<td>860</td>
</tr>
<tr>
<td>20</td>
<td>900</td>
</tr>
</tbody>
</table>


Separator Composition:  \( \text{Na}_2\text{O} = 10\% \)
\( \text{SiO}_2 = 51\% \)
\( \text{Al}_2\text{O}_3 = 36\% \)
after reaching the test temperature. Also, the rate at which the system is brought to temperature has been found to be a factor in obtaining reproducible measurements (ref. 18). Usually a low rate, on the order of several hours of temperature increase, is the most desirable. At this time, there is no reasonable explanation of this phenomenon and optimum conditions must be determined empirically.

3.3.5.5 Volatility

Some salts develop a high vapor pressure well below their normal boiling point. This is an important consideration when using couples with aluminum halides. This condition also necessitates a closed system.

3.3.5.6 Temperature Control

The uniformity of the temperature within the cell is also of prime importance. Therefore, the design of the furnace must limit heat leakage, insure good thermal contact to the cell electrolyte, and prohibit thermal gradients within the electrolyte.

3.3.5.7 Electrical Contact

The making of electrical contact to the reactive anode requires that the material used be inert. This, therefore, limited the material possibilities considerably. In addition, because of a thermoelectric effect (ref. 19) it is desirable to use the same material for electrical contact to both the anode and cathode.

3.3.5.8 Accessibility to Cell Contents

Accessibility to the cell contents during the course of the run is desirable in experimental cells and thus was considered in the cell design.

3.4 EXPERIMENTAL PROCEDURES AND COUPLE MATERIALS INVESTIGATED

The experimental apparatus and the experimental cell for measurements of emf and polarization for the various anode-cathode couples with a molten electrolyte are illustrated in Figure 4. The lower section of this cell was constructed of 40-mm-diameter quartz tubing. This section is connected to a standard taper 50/50 Pyrex ground-glass joint to permit interchange of various
FIGURE 4. IMPROVED EXPERIMENTAL CELL FOR MOLten-SALT STUDY.

ASD-TDR-63-115
electrodes and easy accessibility for the addition of various materials. In this upper section of the cell, there are two joints through which electrical contact is made to the electrodes, a thermocouple well, a gas-release valve, and a three-way stopcock for gas inlet and vacuum outlet.

In order to protect the contents of the cell from atmospheric contamination, purified argon gas (ref. 20, 21) was continually introduced into the cell, and excessive gas pressure was released by means of the pressure-release valve. In order to protect the outside jacket, an inner crucible was added to the electrochemical cell. The composition of the inner crucible was determined by the couple being studied, and is described with the particular couple.

A feeder tube was included in the cell. This tube prevented the exposure of the salts to the atmosphere during the assembly, and thereby prevented moisture absorption. In addition, this tube permitted the addition of the salts after all the components of the cell had been assembled and in this way added to an improved geometry of the electrodes. All these procedures were carried out in a dry box.

A stirrer was incorporated into the cell design in some studies in order that equilibrium could be attained in the system more rapidly.

The circuit diagram for the electrical measurements during charge and discharge is shown in Figure 5.

3.4.1 Preparation of Salts for Electrolyte

In preliminary tests, the salts were stored in a vacuum for a period of three to four days. It was believed that any minute quantity of moisture would be removed in this vacuum. However, after the initial runs, there was evidence of an oxychloride formation in the electrolyte. The erratic results in early studies were attributed, in part, to this. The set-up that was employed for the purification of the salts is presented in Figure 6. The salts were dried in a vacuum oven at 110°C for 24 hours and then mixed thoroughly in a ball mill. The mixture was placed in the filtration apparatus and dry HCl gas was passed over the surface of the powdered salts while the temperature gradually increased. Considerable amounts of water were removed, as was evidenced by the formation of water in the gas outlet tubes.

Once the salts were molten, HCl gas was passed at a vigorous rate until no more water appeared to be evolved. The passage of HCl then continued for two hours, followed by a purge with argon to remove all traces of HCl from the melt. The salts were then filtered, cooled, crushed, and stored in screw-cap jars. Following this processing, the salts were used for
Figure 5. Circuit diagram for the electrical measurements of molten-salt cell during charging and discharging.
FIGURE 6. FILTRATION APPARATUS FOR PURIFICATION OF MOLTEN SALTS.
experiments by taking the required quantities and treating them for a short period of time with HCl gas to remove any adsorbed water on the surface of the eutectic. This experimental precaution, although time consuming, was a necessary factor in obtaining stable potential measurements in molten salt electrolytes.

3.4.2 Experimental Results For Molten-Salt Cells

3.4.2.1 Couples with Molten-Chloride Electrolyte

Mg-AgCl/Ag Couple

The couple Mg-AgCl,Ag was selected to demonstrate the feasibility of couples of the basic types Mg/NaCl, HCl/Ceramic/HCl, MgCl2/C.

Results were obtained on several different experimental cells, as shown in Figure 7 and 8.

The discharge voltage of the Mg-AgCl/Ag couple as a function of current drain is shown in Figure 7. It can be seen that the cell does not polarize appreciably at a given current density as a function of time. The large internal-resistance drop is due to the relatively thick ceramic separator. The data in Figure 7 were obtained on cells which had not been discharged prior to measurement.

Figure 8 shows data obtained with a charge cycle of 15 minutes at 15 milliamperes, followed by a 15-minute discharge. The charge and discharge data for the unplotted cycles are intermediate between the plotted curves. The small degradation in discharge voltage and the increase in charging voltage as a function of the cycle life are attributed to a slow attack on the ceramic separator by the magnesium anode. This effect was indicated by a small amount of darkening of the ceramic separator in the anode compartment after the cell was disassembled.

The cells were operated for a period of 96 hours at a temperature of 700°C before being disassembled for inspection. The only physical change of any of the various cell components was the darkening mentioned above.

Because of the known reversibility of this couple, and the results obtained above, an attempt was made to build a cell on a capacity basis.
FIGURE 7. DISCHARGE VOLTAGE FOR K$_3$-A$_2$Cl/Ag CELL.
The low-ampere-hour capacity of AgCl was recognized. However, the objective of this test was to evaluate the system as a power cell. The electrochemical structure of this cell was as follows:

\[ \text{Mg/MgCl}_2, \text{NaCl/ceramic/MgCl}_2, \text{NaCl,AgCl/Ag} \]

The experimental arrangement and description of the couple are given below:

**Electrodes:**
- **Anode** .25 gram magnesium, molten
- **Cathode** 3.8 grams silver powder, pressed on a silver grid, and anodized in 2M HCl

**Electrolyte (Excess):**
- **Anolyte** MgCl\(_2\), NaCl (48, 52 mole-%)
- **Catholyte** MgCl\(_2\), NaCl, AgCl (45, 50, 5 mole-%)

**Separator** Ceramic tube (approximate area of 1.32 square inches)

**Operating** 700°C

Figure 9 shows the geometric configuration of this cell. This cell was discharged at a current of 40 mA, and the discharge curve of this cell, at 40 mA, is presented in Figure 10. The curve shows that the cell voltage dropped rapidly with respect to discharge rate and time. Since these results showed no improvement over this couple when solid-silver sheet was used, the experiment was discontinued.

**The Li-AgCl/Ag Couple**

To demonstrate the reversibility of lithium as an anode material, a Li-AgCl/Ag couple was fabricated.

This test cell was fabricated with molybdenum tube inserted inside the upper portion of the ceramic separator tube. The molybdenum insert was to protect the ceramic from attack by the molten lithium metal which floats on the electrolyte. Lithium forms the commonly observed metal "fog" which makes the selection of the electrolyte critical. Lithium ions also reduce the ionic conductivity of the
FIGURE 9. CELL CONFIGURATION OF Mg-AgCl/Ag MOLTEN-SALT BATTERY.
ceramic, thereby decreasing the efficiency of the couple under investigation. A possible solution to this problem is presented in Section 3.5.4. The molybdenum tube helps to protect the ceramic from this contamination. Figure 11 illustrates the configuration of the ceramic separator tube.

The configuration of this cell was as follows:

\[ \text{Li/LiCl , NaCl/ceramic/MgCl}_2 \ , \text{ NaCl,AgCl/Ag} \]

The experimental arrangement and description of this couple are given below:

Electrode:
- Anode: 0.1 gram lithium
- Cathode: 0.005 gram silver plated on one square inch of platinum

Electrolyte (Excess):
- Anolyte: LiCl, NaCl (60, 40 mole-%)
- Catholyte: NaCl, MgCl\(_2\), AgCl (50, 45, 5 mole-%)

Container: Quartz insert
Separator: Ceramic tube (approx. area of 1.32 square inches)
Operating Temperature: 700°C

Representative charge and discharge cycles of this cell are presented in Figure 12. The cell was cycled twice at a current of 10 mA, and reversibility was exhibited. The open-circuit voltage of this cell was 2.10 volts, which is 0.60 volts lower than the theoretical open-circuit voltage. At this time, there is no acceptable explanation for the low voltage.

The Mg-NiCl\(_2\)/Ni System

The geometric configuration of this cell is the same as illustrated in Figure 11. This system enables the use of the MgCl\(_2\), NaCl eutectic as the electrolyte for both compartments of the cell.
FIGURE 11. MOLYBDENUM INSERT TUBE ARRANGEMENT FOR Li-AgCl/Ag COUPLE.
FIGURE 12. CHARGE AND DISCHARGE DATA FOR Li-AgCl/Ag COUPLE.
Hence, the melting point of the magnesium anode (650°C) need not be exceeded to bring the electrolyte to its molten state since the melting point of the electrolyte is 450°C. The advantage of this system is that the surface area per unit weight of magnesium can be greatly increased by the design of the electrode. However, when the magnesium is molten, the system is limited to the surface area of a sphere.

Electrochemically the couple was set up as follows:

\[ \text{Mg/MgCl}_2, \text{NaCl/ceramic/MgCl}_2, \text{NaCl, NiCl}_2/\text{Ni} \]

The cell is described quantitatively below:

Electrodes:

Anode \( \text{Mg} = .5 \text{ gram; surface} = 2 \text{ square cm.} \)
Cathode \( \text{Ni sheet} = 2 \text{ gram; surface} = 10 \text{ square cm.} \)

Electrolyte (Excess):

Anolyte & Catholyte \( \text{MgCl}_2, \text{NaCl (48, 52 mole-\%)} \)
Separator - Ceramic Tube: area = 1.32 square inches.
Operating Temperature \( 500°C. \)

An initial discharge curve at 20 ma is shown in Figure 13.

The \( \text{Mg-CuCl}_2/\text{Cu(Pd)} \) Couple

A cell constructed with the configuration:

\( \text{Mg/MgCl}_2, \text{NaCl/ceramic/MgCl}_2, \text{NaCl, CuCl/Cu(Pd)} \)
was chosen to demonstrate the reversibility of a CuCl/Cu cathode.

The experimental arrangement and description of this couple are given below:

Electrodes:

Anode \( 0.6 \text{ gram magnesium} \)
Cathode \( 1.000 \text{ gram, copper plated on one square centimeter of palladium, plus .002 gram CuCl added to the melt.} \)
FIGURE 13. DISCHARGE DATA FOR Mg-NiCl₂/Mn MOLTEN-SALT CELL.
**Electrolyte (Excess):**

- **Anolyte:** \( \text{MgCl}_2, \text{NaCl} \) (48, 52 mole-%)
- **Catholyte:** \( \text{MgCl}_2, \text{NaCl, CuCl} \)

**Container:** Quartz Tube

**Separator:** Ceramic tube (area = 1.32 square inches).

**Operating Temperature:** 700°C.

Typical charge and discharge data for this couple are shown in Figure 14 and Table V. A base material, such as platinum or palladium, was required because of the large exchange currents often encountered with many electrode combinations in molten-salt systems (ref. 2). In this test, palladium was used in place of platinum as the base cathode material in order to eliminate the alloying effect previously encountered.

At 700°C, the theoretical reversible potential of this couple is 1.45 volts. However, the data indicate that the potential of this experimental cell was 1.65 volts. The higher potential did not affect reversibility at charge and discharge currents of five milliamperes.

**The Al-NiCl\(_2\)/Ni Couple**

A cell of the configuration \( \text{Al} / \text{AlF}_3, \text{NaCl/ceramic/NaCl, MgCl}_2/\text{Ni(Pt)} \) was chosen to demonstrate the reversibility of a \( \text{Al}/\text{NiCl}_2/\text{Ni} \) couple. The reversible potential of this couple is 1.35 volts at 700°C. Experimentally, the couple demonstrated its reversible potential.

The experimental arrangement and description of this couple are as follows:

**Electrodes:**

- **Anode:** 0.5 gram of aluminum
- **Cathode:** 0.005 gram nickel, plated on one square inch of platinum

**Electrolyte (Excess):**

- **Anolyte:** \( \text{AlF}_3, \text{NaF} \) (60, 40 mole-%)
- **Catholyte:** \( \text{NaCl, MgCl}_2, \text{NiCl}_2 \) (51.8, 47.8, 0.4 mole-%)
FIGURE 14. CHARGE AND DISCHARGE DATA FOR A Mg-CuCl/Cu COUPLE. TEMPERATURE = 700°C.
TABLE V. CHARGE AND DISCHARGE DATA OF Mg-CuCl/Cu(Pd) COUPLE.

<table>
<thead>
<tr>
<th>TIME (Minutes)</th>
<th>CHARGE DATA AT 5 MA (Volts)</th>
<th>DISCHARGE DATA AT 5 MA (Volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CYCLE</td>
<td>CYCLE</td>
</tr>
<tr>
<td>Initial</td>
<td>1.78 1.86 2.14</td>
<td>1.65 1.68 1.80</td>
</tr>
<tr>
<td>1</td>
<td>- - -</td>
<td>1.56 1.59 1.55</td>
</tr>
<tr>
<td>5</td>
<td>2.24 2.25 2.20</td>
<td>1.49 1.51 1.48</td>
</tr>
<tr>
<td>10</td>
<td>2.26 2.25 2.21</td>
<td>1.42 1.46 1.45</td>
</tr>
<tr>
<td>15</td>
<td>2.26 2.26 -</td>
<td>1.37 1.42 1.42</td>
</tr>
<tr>
<td>20</td>
<td>2.26 2.26 2.24</td>
<td>- 1.39 1.40</td>
</tr>
</tbody>
</table>
Container Quartz tube
Separator Ceramic tube (area = 1.32 square inches)
Operating Temperature 700°C.

Four charge and discharge cycles, at a current of 10 ma, were performed on this couple. As may be observed from Figure 15, the cell behaved reversibly with respect to the charge and discharge currents of 10 ma. Additional experimental tests were conducted on this couple in order to measure its coulombic capacity and efficiency. Its estimated theoretical capacity is 238 watt-hours per pound.

The Al₃⁺, AgCl/Ag Couple

This couple was chosen to demonstrate the reversibility of an aluminum anode. The configuration and physical description of this couple are as follows:

Al/AlF₃, NaF/ceramic/MgCl₂, NaCl,AgCl/Ag(Pt)

Electrodes:
Anode 0.05 gram of aluminum
Cathode 0.005 gram of silver, plated on one square inch of platinum

Electrolyte (Excess):
Anolyte AlF₃, NaF (60, 40 mole-%)
Catholyte MgCl₂, NaCl, AgCl (45, 50, 5 mole-%)

Container Quartz tube
Separator Ceramic tube (approx. area = 1.32 square inches)
Operating Temperature 800°C.

The charge and discharge curves for this couple are presented in Figure 16. The cell was charged and discharged at currents of 5 and 10 ma. Under these two conditions the cell behaved reversibly as predicted. The theoretical capacity of this couple is 151 watt-hours per pound of reactant material.
FIGURE 16. CHARGE AND DISCHARGE DATA AT VARIOUS CURRENTS FOR Al-AgCl/Ag COUPLES.
The Mg/NiO, Ni Couple

A cell having the configuration:

\[ \text{Mg/MgCl}_2, \text{NaCl/ceramic/Li}_2\text{SO}_4, \text{Na}_2\text{SO}_4, \text{CaO/NiO, Ni} \]

was chosen to demonstrate the feasibility of a sulfate-eutectic electrolyte, and to demonstrate reversibility of an oxide cathode. The reversibility of NiO,Ni under no-load conditions has been demonstrated. The experimental arrangement and description of this couple follows:

Electrodes:
- Anode: 1.5 gram of magnesium
- Cathode: 0.5 gram of nickel

Electrolyte (Excess):
- Anolyte: MgCl\(_2\), NaCl (48, 52 mole-%)
- Catholyte: Li\(_2\)SO\(_4\), Na\(_2\)SO\(_4\), CaO (70.6, 28.4, 1.0 mole-%)


Separator: Ceramic tube (area = 1.32 square inches)

Operating Temperature: 600°C.

Typical charge and discharge data for this couple are presented in Figure 17. The cell was cycled 10 times for periods of 15 minutes each at charge and discharge currents of 5 milliamperes.

The cell demonstrated its reversible potential of 1.45 volts, and was reversible under load, as shown by Figure 17.

The Mg-Cu\(_2\)O, Cu(Pd) Couple

A cell having configuration:

\[ \text{Mg/MgCl}_2, \text{NaCl/ceramic/Li}_2\text{SO}_4, \text{NaSO}_4, \text{CaO/Cu}_2\text{O, Cu(Pd)} \]

operating at a temperature of 600°C, demonstrated the reversibility of a Cu\(_2\)O/Cu electrode.
FIGURE 17. CHARGE AND DISCHARGE DATA FOR NIO-NiO/Ni COUPLE.
The physical arrangement of this cell is as follows:

Electrodes:

<table>
<thead>
<tr>
<th>Anode</th>
<th>0.8 gram of magnesium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>1.000 gram of copper, plated on one square cm of palladium, plus .002 gram of Cu$_2$O added to the melt.</td>
</tr>
</tbody>
</table>

Electrolyte (Excess):

<table>
<thead>
<tr>
<th>Anolyte</th>
<th>MgCl$_2$, NaCl (48, 52 mole-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catholyte</td>
<td>Na$_2$SO$_4$, Li$_2$SO$_4$, CaO (70.6, 28.4, 1.0 mole-%)</td>
</tr>
</tbody>
</table>

Separator | Ceramic tube (area = 1.32 square inches) |

Operating Temperature | 600°C. |

Discharge and charge data for this couple are presented in Figure 18 and Table VI. This cell attained its theoretical reversible potential of 1.40 volts at 600°C. The cell was cycled five times at a current of five milliamperes, and, as can be observed from the data in both the figure and the table, the cell exhibited reversibility under load conditions.

The Al-Ni$_{2+x}$ Couple

The Al-Ni$_{2+x}$/Ni system was designed to function as a power cell because it was anticipated that this couple would be used for a prototype molten-salt secondary battery. The experimental arrangement and the qualitative and quantitative materials used in this couple are given below:

\[ \text{Al/AlF}_3, \text{NaF/ceramic/Na}_2\text{SO}_4, \text{MgSO}_4/\text{NiO}, \text{Ni} \]

Electrodes:

<table>
<thead>
<tr>
<th>Anode</th>
<th>3.5 gram of aluminum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>Two sintered-nickel plates, containing a total of 6 grams of pure Ni and 4 grams of Ni$_{2+x}$</td>
</tr>
</tbody>
</table>
FIGURE 18. CHARGE AND DISCHARGE DATA FOR Mg-Cu₂/Cu COUPLE. TEMPERATURE = 600°C.
TABLE VI. CHARGE AND DISCHARGE DATA OF Mg-Cu₂/O/Cu COUPLE.

<table>
<thead>
<tr>
<th>TIME (Minutes)</th>
<th>CHARGE DATA AT 5 MA (Volts)</th>
<th>DISCHARGE DATA AT 5 MA (Volts)</th>
<th>CYCLE</th>
<th>TIME (Minutes)</th>
<th>CYCLE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>3</td>
<td>5</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Initial</td>
<td>1.00</td>
<td>0.87</td>
<td>0.47</td>
<td>Initial</td>
<td>1.12</td>
</tr>
<tr>
<td>5</td>
<td>1.37</td>
<td>1.49</td>
<td>1.10</td>
<td>1</td>
<td>0.70</td>
</tr>
<tr>
<td>10</td>
<td>1.40</td>
<td>1.52</td>
<td>1.53</td>
<td>2</td>
<td>0.62</td>
</tr>
<tr>
<td>15</td>
<td>1.41</td>
<td>1.53</td>
<td>1.60</td>
<td>3</td>
<td>0.54</td>
</tr>
<tr>
<td>20</td>
<td>1.42</td>
<td>-</td>
<td>1.59</td>
<td>4</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>9</td>
<td>-</td>
</tr>
</tbody>
</table>
Electrolyte (Excess):

Catholyte \( \text{Na}_2\text{SO}_4, \text{MgSO}_4 \) (56, 4\% mole-%)

Anolyte \( \text{AlF}_3, \text{NaF} \) (50, 50 mole-%)

Separator Ceramic tube (area = 1.32 square inches)

Operating Temperature 800°C.

Figure 19 illustrates the configuration of this power cell. Figure 20 presents the discharge data of this cell at 12 and 50 mA, and Figure 21 represents its charge and discharge data at various currents. The data indicate the possibility of designing a power electrode for the present application by increasing the surface area of the cathode.

However, because of an apparent attack on the ceramic tube by the fluoride electrolyte, and the high temperature required to bring the electrolyte to its molten state, the examination of this system was discontinued.

The Mg-NiO/Ni System

The geometric configuration of this cell is the same as shown in Figure 19, although the anode and anolyte are different in this case.

The description of the couple appears below:

\[ \text{Mg/MgCl}_2, \text{NaCl/ceramic/MgSO}_4, \text{Na}_2\text{SO}_4/\text{NiO}, \text{Ni} \]

Electrodes:

Anode 2 gram molten magnesium

Cathode Sintered-nickel plates, containing a total of 4 grams NiO and 6 grams Ni.

Electrolyte (Excess):

Anolyte \( \text{MgCl}_2, \text{NaCl} \) (48, 52 mole-%)

Catholyte \( \text{MgSO}_4, \text{Na}_2\text{SO}_4 \) (44, 56 mole-%)

Separator Ceramic tube (area = 1.32 square inches)

Operating Temperature 800°C.
FIGURE 19. CELL CONFIGURATION FOR Al-NiO/H1 MOLTEN-SALT COUPLE.
FIGURE 20. DISCHARGE DATA FOR Al/Na/Na COUPLE.
FIGURE 21. FIRST-CYCLE CHARGE AND DISCHARGE DATA FOR AL/NaO/Na COUPLE.
The charge and discharge results for this couple appear below:

Open Circuit Voltage (o.c.v.) = 1.60v

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Voltage (volts)</th>
<th>Current (ma)</th>
<th>Time (minutes)</th>
<th>Voltage (volts)</th>
<th>Current (ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.40</td>
<td>100</td>
<td>0</td>
<td>1.65</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>.70</td>
<td>100</td>
<td>1</td>
<td>1.70</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>100</td>
<td>7</td>
<td>1.75</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>1.36</td>
<td>20</td>
<td>10</td>
<td>1.76</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>1.30</td>
<td>20</td>
<td>10</td>
<td>1.80</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>.80</td>
<td>20</td>
<td>20*</td>
<td>2.25</td>
<td>20</td>
</tr>
</tbody>
</table>

*Contact was broken at the cathode after 20 minutes of charge.

Work was discontinued on this cell because of its inability to accept high charge and discharge rates without considerable polarization. A power cell with a molten anode is considered impractical because of the small surface area per unit weight of the anode. This results in a high-current density and, thus, considerable anode polarization.

3.5 CERAMIC SEPARATOR STUDY

3.5.1 Objective

The objective of this study was to determine the behavior of the ceramic material under consideration with respect to its use in a molten-salt battery. The following factors were considered in this study:

a. stability with respect to anode material.

b. sensitivity of the conduction mechanism to environment.

c. sensitivity of current reversibility to electrolyte impurities.
d. effect of mass transport on cell design.

e. temperature gradient in the separator.

f. thermal coefficient of expansion.

g. other elements having high ion mobility.

3.5.2 Ceramic Tube and Disc Preparation

Many ceramic-separator tubes and discs were prepared for use in experimental cells. The materials used in the preparation of the ceramic slip carried with them many impurities (Fe₂O₃, Al₂O₃, CaO, MgO) which are detrimental to the system, particularly in reducing the diffusion rate of the sodium ion. To minimize the effects of the impurities, a ceramic was developed to eliminate the need for Old Mine Kentucky Ball clay and Pioneer Georgia kaolin clay. These clays contain potassium and iron in sufficient quantities to have detrimental effects on the systems under investigation. The chemical compositions of these two clays are as follows:

<table>
<thead>
<tr>
<th>Material</th>
<th>Kentucky Ball (%)</th>
<th>Georgia Kaolin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>51.92</td>
<td>45.34</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>31.78</td>
<td>37.29</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.52</td>
<td>1.54</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>.869</td>
<td>.61</td>
</tr>
<tr>
<td>CaO</td>
<td>.21</td>
<td>.25</td>
</tr>
<tr>
<td>MgO</td>
<td>.19</td>
<td>.22</td>
</tr>
<tr>
<td>Na₂O</td>
<td>.38</td>
<td>.35</td>
</tr>
<tr>
<td>K₂O</td>
<td>.89</td>
<td>.10</td>
</tr>
<tr>
<td>Ignition Loss</td>
<td>12.29</td>
<td>13.38</td>
</tr>
</tbody>
</table>

Because of the elimination of these clays, a different casting procedure was used. This new procedure used toluene as a casting medium, and permitted the ceramic tube to be cast without the addition of clays to provide workability. The ceramic tubes and discs were then fired in an electric furnace at a pyrometric-cone equivalent to two (nominal temperature for heating cycle is 1170°C.)
3.5.3 Procedure for Preparation of Ceramic Separator

A doctor blade, which is a precision blade that uses a micrometer adjustment for positioning blade height, was used to fabricate ceramic separators in thin sheets. The ceramic disc used was prepared using the following formula:

\[
\begin{align*}
\text{Sodium Silicate (Na}_2\text{SiO}_3) & \quad 128 \text{ g} \\
\text{Alumina (Al}_2\text{O}_3) & \quad 107 \text{ g} \\
\text{Silica (SiO}_2) & \quad 117 \text{ g} \\
\text{Kentucky Ball} & \quad 54 \text{ g} \\
\text{Georgia Kaolin} & \quad 71 \text{ g}
\end{align*}
\]

This mixture was then calcined for 30 minutes at 1100°C, followed by pulverizing of the frit in a grinder. To the pulverized material, 142 g of Kentucky Ball, 111 g of Georgia Kaolin, and 350 cc of water were then added. This mixture was milled and passed through a ferro-filter in order to remove any traces of iron which may have been picked up in the grinding process.

After drying in an oven at 100°C, the material was mixed with an organic binder (WYNC, a mixture of polyvinyl acetate and polyvinyl chloride) and a solvent carrier (methyl ethyl ketone). This material was then cast by means of the doctor-blade process into a thin film (.005 - .01-inch), laminated to the desired thickness, and fired to 1170°C for one hour on zirconia setters.

The initial work in this study was aimed at the forming or cutting, of the ceramic disc prior to firing of the body. The tolerances necessary for the final piece, with respect to the diameter of the disc, dictated forming (cutting) after fixing. This was accomplished by means of ultrasonic cutting.

3.5.4 Studies of Ceramic Separator

Various fundamental studies of the ceramic separator were performed. These studies were conducted to consider corrosion by the salts (both under static and dynamic conditions), as well as dc conductivity of the separator.

Corrosion was measured by carefully predetermining the dimensions of the ceramic, exposing the ceramic to the molten salt for a given period of
time, cooling (to solidify the salt around the ceramic), and cross sectioning through the ceramic. This allowed careful measurement to be made of the area of ceramic exposed to the salt. From those measurements a corrosion rate was established.

A dc conductivity bridge was used to calculate specific resistance of the ceramic separator. Standard electrochemical conductivity test procedures were followed. Based on these data it was ascertained that a specific change improves the quality. When the nature of sodium-ion mobility had been carefully studied, other materials were studied. All the monovalent cations in the IA group of the Periodic Chart were considered.

It is well known that the diffusion rate of potassium is lower than sodium. A possible explanation is the difference in ionic diameters. Pauling has calculated the diameters of sodium and potassium to be 1.90 Å and 2.66 Å respectively. From these diameters, potassium is volumetrically 2.8 times larger than sodium. Therefore, more force is required to initially move a potassium ion, and, according to Taylor (ref. 27) the specific resistance will be higher, as shown in the following equation:

\[
\log \rho = \frac{HC + A}{RT}
\]

where
\(\rho\) = specific resistance
\(A\) = a constant for a given glass
\(HC\) = energy of activation
\(R\) = the gas constant
\(T\) = absolute temperature

It can be seen from this equation that an ion having a larger diameter, and thus having a higher activation energy, will have a higher specific resistance. The dc conductivity, the inverse of specific resistance, will be lower. It is also apparent that an increase in temperature will result in an increase in dc conductivity.

Candidates for this study were selected according to the following characteristics:

a. Monovalence - The direction of movement is in opposition to electric charge; therefore, it is improbable that divalent ions, even smaller ionic diameters, are able to migrate at temperatures where the monovalent ions diffuse. Divalent ions, such as calcium in ziconates, were studied to verify this theory.
b. Ionic diameter smaller than 1.90 Å - These ions require lower energy for activation, and, therefore, have lower specific resistance and higher dc conductivity.

Based on the above criteria, lithium was selected as the most logical candidate. Lithium is a monovalent ion with an ionic diameter, as calculated by Pauling, of 1.20 Å. This volumetrically is less than 1/2 that of sodium; hence, it requires a lower activation energy resulting in a lower specific resistance and a higher dc conductivity. Lithium is most desirable because it produces a minimum-weight electrolyte. The use of lithium resulted in a ceramic separator material which permitted rapid diffusion at a relatively low activation level and provided a cell capable of operating satisfactorily at a lower temperature.

3.5.4.2 Thermal Coefficient of Expansion

Initial findings indicated that the thermal coefficient of expansion of the ceramic material is of prime importance in sealing the separator to the experimental cell design. This fact was particularly important in the physical design of the cell, developed to demonstrate the capacity of a selected couple.

The thermal coefficient of expansion of the ceramic separator is shown in Figure 22. This curve shows that the thermal coefficient of expansion of the ceramic is approximately 10 times that of fused quartz. The thermal coefficient of expansion of this ceramic material is very similar to that of standard ceramic bodies, and caused a severe separator-to-battery-housing sealing problem. The solution to this is discussed in Section 3.6.2.3.

3.5.4.3 Improvement of the Ionic Conductivity of the Ceramic Separator

In an electrochemical cell utilizing molten-salt electrolyte, it is essential that the ceramic separator be chemically and thermally resistant and possess a high degree of "transparency" to the movement of the sodium ion. By means of present techniques, it was possible to prepare a ceramic separator which permitted mobility of potassium, silver, or lithium ions.

Improvement of the ceramic separator characteristics was attempted in two areas. These were:

a. improving the present ceramic body by introducing the soda $(Na_2SiO_3)$ in another form and the removing of the ball and
FIGURE 22. COMPARISON OF THE THERMAL COEFFICIENT OF EXPANSION OF 10% \( \text{Na}_2\text{O} \) CERAMIC BODY AND FUSED QUARTZ.
kaolin clay. The main purpose in adding these clays was for the plasticity required in slip casting. However, in the method now used to prepare the ceramic separation disc (Section 3.5.3), the organic (toluene) binder replaces these clays. The removal of these clays from the procedure eliminated any contaminants from the clays.

b. investigating other ceramics capable of permitting mobility of a single ion of other elements from the IA group of the periodic chart.

Examples: lithium, potassium

3.5.5 Corrosion Studies

In the design of a molten-salt secondary battery, the corrosion rate of the molten salt on the various materials used in the battery construction must be known. A corrosion study which exposed the various materials to the molten salts for approximately one week was initiated.

3.5.5.1 MgCl₂, NaCl on Frenchtown 4462 Alumina

A corrosion study was made on Frenchtown 4462 alumina since the prototype battery was designed to be contained in an alumina cylinder. The alumina was cross sectioned after four days exposure to a molten MgCl₂, NaCl electrolyte. Although a slight decrease in the outer skin thickness was observed, no definite conclusions regarding corrosion could be made from these initial tests.

3.5.5.2 MgCl₂, NaCl on Corning 7280 Glass

Corning 7280 glass was considered for use in sealing various joints. This glass was subjected to the molten salt for two hours in an argon atmosphere, and significant changes were observed. The previously clear glass became very cloudy, the weight increased slightly, and the size was reduced slightly. Cross-section studies show definite attack by the salt. When this attack was recognized, attempts were made to make seals with another sealer. Although a successful try was made to seal the ceramic separator directly to the alumina by means of green ceramic slip, this method was discarded in favor of the procedure described in Section 3.6.2.2.
5.5.3 MgCl₂,NaCl on the Ceramic Separator (10-percent Na₂O)

The ceramic separator showed no evidence of corrosion by the MgCl₂,NaCl electrolyte.

3.5.6 Resistivity Studies

3.5.6.1 Cell Configuration for Resistivity Measurement

It was necessary that the resistivity of the ceramic separator be determined in the design of a molten-salt secondary battery. A cell was designed for the purpose of determining the resistivity of the ceramic separator. Figure 23 illustrates the cell configuration used to obtain this resistivity measurement.

The cell was constructed with a 3/4-inch diameter by 10-inches long Corning 7280 glass tube. Three platinum electrodes were placed equidistant from each other in the glass tube, and the ceramic separator was placed between two of the electrodes. The electrolyte used in this cell design was a 48,52 mole-percent MgCl₂,NaCl eutectic. An ac bridge was used to measure the cell resistance.

3.5.6.2 Resistivity Data

The value of the resistance of the ceramic separator was obtained by subtracting the difference between the cell resistance, measured with the ceramic separator, and the cell resistance measured without the ceramic separator.

\[
\rho = \frac{R \cdot A}{L}
\]

where:

\[\rho\] = resistivity (ohms/cm)

\[A\] = area of electrode (cm²)
\[ l = \text{distance between electrodes, for salt resistivity (cm)} \]
\[ l' = \text{thickness of ceramic separator, for separator resistivity (cm)} \]
\[ R = \text{resistance (ohms)} \]

Table VII shows the data obtained for the resistivity of the ceramic separator and salt. The data indicate that the ceramic separator is the limiting factor with respect to resistivity, but not necessarily to the resistance of a molten-salt secondary battery. Figure 24 presents a plot of the resistivity of the ceramic separator versus temperature.

Since the molten-salt electrolyte has finite resistivity, the area of the electrodes and the distance between them must be considered in any design of a practical molten-salt secondary battery for space applications.

3.6 MOLten-SALT SECONDARY BATTERY DESIGN

A molten-salt secondary battery was fabricated upon conclusion of the present program. This battery consisted of two cells in series. The design objectives of this battery were as follows:

a. capable of a 20-ampere discharge for 35 minutes with voltage maintained at 2.6 volts, ±20 percent.

b. capable of repeated cycling (a minimum of five cycles).

c. a minimum battery weight which is a function of design.

d. a minimum battery volume as a function of design.

e. capable of operation in any position.

f. capable of operation at zero gravity.
TABLE VII. RESISTIVITY DATA OF THE CERAMIC SEPARATOR (DATA OBTAINED FROM TWO DIFFERENT CELLS).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Resistivity (ohm-cm)</th>
<th>Resistivity (ohm-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Salt</td>
<td>Separator</td>
</tr>
<tr>
<td>500</td>
<td>1.1</td>
<td>417</td>
</tr>
<tr>
<td>510</td>
<td>1.1</td>
<td>160</td>
</tr>
<tr>
<td>525</td>
<td>1.1</td>
<td>-</td>
</tr>
<tr>
<td>570</td>
<td>1.0</td>
<td>-</td>
</tr>
</tbody>
</table>

Pt electrode area = 0.8 cm²
Pt electrode distance = 4.45 cm
Pt electrode area = 1.0 cm²
Pt electrode distance = 3.81 cm

ASD-TDR-63-115 57
3.6.1 Electrodes

3.6.1.1 Anode

The battery used magnesium as the anode. Magnesium was selected in preference to aluminum because the fluoride eutectic electrolyte, which is necessary with an aluminum anode attacks the ceramic separator. Magnesium also permitted the use of a MgCl₂-NaCl eutectic electrolyte. If aluminum had been used, the use of a AlF₃-NaF eutectic which has a melting point of 690°C would have been required. This temperature is well above the desired operating temperature of the battery. Therefore, the use of a MgCl₂-NaCl eutectic, whose melting point is 450°C, permitted the operation of the battery within a reasonable temperature.

3.6.1.2 Cathode

A cathode made of either NiO or NiCl₂ would provide the highest ampere-hour and watt-hour per unit weight of material. The NiCl₂ cathode was chosen because it permitted the use of a chloride electrolyte (MgCl₂-NaCl) instead of a sulfate electrolyte which would have been required if an oxide cathode, such as NiO, were selected. The melting point of the sulfate electrolyte is greater than the melting point of the magnesium electrode. Therefore, a sulfate electrolyte was undesirable because it would necessitate the use of a molten, rather than a solid, anode. The battery was designed to operate at a minimum of 450°C (melting point of electrolyte) and a maximum of 650°C (melting point of magnesium).

3.6.2 Mechanical Design

3.6.2.1 Geometry

The geometry of the cell was limited by the size to which the ceramic separator could be fabricated. The cell was designed to produce a minimum resistance of the separator and molten-salt. A 3.5-inch-diameter ceramic separator with a minimum thickness of 0.015-inch was the largest size of ceramic separator that could currently be made.

The cells were cylindrical in shape with a radius of about 3.5 inches. The distance between the electrodes was approximately 0.5-inch.

Electrolyte volume was critical because cycling involved a transfer of NaCl toward the cathode and affected the mole percent and the melting point of the electrolyte.
Brazing Technique: One BT-alloy washer (0.900-inch ID, 1.125-inch OD and 0.005-inch thick) was used for each braze. To facilitate wetting, a 3/8-inch-wide band was nickel plated around the center hole in the seal cover. The shoulder of the pour hole was also nickel plated. Nickel approximately 0.001-inch thick was used. These brazes were made in the same Hoskins furnace with a live hydrogen atmosphere. The braze zone was operated at 800°C. A 10-minute preheat, 25-minute braze, and two-hour cooling cycle was used.

Assembly Braze

Set Up: The ceramic separator was mounted between the alumina cylinders and the cylinders joined with 7/16-inch wide, 0.005-inch thick Kovar band, cut long enough to permit a 1/2-inch overlap and plated with .002-inch nickel to facilitate wetting of the braze.

Before brazing, a ceramic separator was placed between two cylinders, each of which had shoulder pieces attached. A BT-brazing alloy strip, wider and longer than the Kovar band, was wrapped around the joint between the two cylinders. The Kovar band was wrapped over the BT-alloy. After centering the bands over the metalized area on the cylinders, they were bound snugly by wrapping the outside with several turns of .020-inch nickel wire. Two turns of .015-inch BT-alloy wire were wrapped around each edge of the Kovar strip to provide supplementary braze material to insure a fillet at the edge. A two-turn wrapping of .020-inch molybdenum wire was made at the lower edge of the metalized area. This wrapping prevented the Kovar band from slipping as the braze material melted.

Brazing Technique: Previous experience had demonstrated the necessity of heating the ceramic separators slowly to prevent cracking. The assembly braze was made in a periodic-type furnace of RCA design which could be heated and cooled slowly. This furnace had an Inconel muffle approximately 8 x 12 x 36 inches and was Globar heated. The maximum power consumption was 40 KVA. Separate top and bottom temperature controllers were provided.

For brazing, the assembly was located centrally in the muffle by blocking it up on stainless steel supports. The furnace was closed and flushed with dry hydrogen at a flow rate of 15 to 18 cubic feet per hour. After 30 minutes, the furnace was heated to 500°F, held 15 minutes, raised to 750°F, and held for 15 minutes. This schedule was continued to 1500°F, using 250°F increments and 15-minute holds. After the hold at 1500°F, the temperature was raised to 1700°F and held for 30 minutes. The cooling program duplicated in reverse the cycle used for heating. The dry-hydrogen flow was maintained throughout the heating and cooling cycles.
ONE-HALF OF MOLTEN-SALT SECONDARY CELL. CONSTRUCTION OF NICKEL ELECTRODE IS SHOWN.

MOLTEN-SALT SECONDARY CELL, PRIOR TO ADDING END CAPS TO COMPLETE CONSTRUCTION.

COMPLETED MOLTEN-SALT SECONDARY CELL.
The amount of sodium chloride transferred is a function of the extent of cell charge or discharge. In the battery, the amount of electrolyte was equal to the minimum amount required to maintain the NaCl: MgCl₂ ratio and to keep the electrolyte molten at 550°C at all states of charge. This necessitated a volume of electrolyte of approximately 10 cubic inches. Since the diameter of the cell was fixed at 3.5 inches, the minimum width of both the anode and cathode compartments was limited to one inch. If the electrodes were kept two inches apart, the voltage drop would be excessive because of the resistivity of the molten-salt. In order to provide a sufficient quantity of electrolyte, without a large voltage drop, the cell configuration shown in Figure 25 was designed.

3.6.2.2 Fabrication Methods

Kovar Shoulder-to-Alumina Cylinder Braze

Jigging: To center the alumina cylinders, or the Kovar shoulder pieces, small nickel tabs were spot welded to the Kovar. Three or four tabs, which measured approximately 3/16 x 1/2 x .005 inches, were bent perpendicular to the Kovar to form a nest into which the cylinder was inserted. The braze material was melted, and the nickel tabs were brazed rigidly into place.

An external clamp made from 1/2-inch-thick cold-rolled steel was used to prevent the Kovar shoulder piece from warping during the braze cycle. To prevent the brazed assembly from sticking to the clamp, a powdered alumina release agent was painted on the clamping surfaces.

Brazing Technique: Two copper washers, 3-inch ID, 3-1/2-inch OD and 0.005-inch thick were used to make each braze, and were held in place by the nickel tabs which centered the alumina cylinders.

The brazing was done in a Hoskins-type furnace using a hydrogen atmosphere. This furnace is a push-through type with preheat, braze, and cooling zones. The braze zone was operated at 1130°C to make these copper brazes. The heating cycle was: 10 minutes in preheat zone, 25 minutes in braze section, and two hours in cooling zone.

Pour Hole-to-Seal Cover Braze:

The pour hole piece was designed with a shoulder so that it was self jiggling in the center hole of the Kovar seal cover. To prevent the seal cover from warping, a similar clamping jig to that described above was used with a release agent to prevent sticking.
FIGURE 25. CELL CONFIGURATION OF Mg-NiCl$_2$/Ni MOLten-SALT SECONDARY BATTERY.
**Electrode Attachment:** Electrode spiders were welded to the Kovar shoulders with an ASCO 20-KVA spot welder, model MXFR20-18. A one-second weld time was used with 3/16-inch diameter electrodes, at a transformer setting of two. It is essential in welding the spiders that intimate contact be maintained between the metal parts before the power is applied. Poor contact will result in a weak weld or a burn-through in the material.

**Seal Cover-to-Shoulder Heliarc Weld**

**Jigging:** The seal covers with pour holes were heliarc-welded to the shoulders. A jig was used which was designed to keep heat from reaching the brazed joint between the alumina cylinder and the shoulder piece. This jig also supplied sufficient load to the Kovar sheets to keep them flat and in intimate contact. Two spacer washers were used on each end to build up the edge thickness to compensate for the electrodes. The jig was mounted on a turntable which rotated at about 1.3 rpm.

**Welding:** A Miller, Model 320A BP-La, ac-dc, inert-gas welder was used for this operation. It was operated on straight-polarity dc on the 10-160-ampere tap with a current setting of 54. An Argon gas flow of 10 cubic feet per hour was used. The high-frequency start and remote-control operational modes were used.

After the piece was centered on the turntable, the electrode was mounted about 1/16-inch from the edge of the Kovar pieces. The turntable was started, and the arc was struck. Minor adjustments to the arc intensity were made by the operator who used a foot-control switch. As the turntable rotated slowly, the arc melted the four thickness of Kovar and made a perfect weld joint.

**Pour-Hole Sealing**

The male and female pour-hole pieces were designed with narrow ridges on the mounting surfaces. When the insert was tightened against the gold seal ring, these ridges cut into the soft gold and formed an hermetic seal. Gold was selected because of its ductility and its ability to cold weld to the stainless under high pressures. Joints with this basic design have been used in high-vacuum systems where the demountable feature is required.
3.6.3 **Electrochemical Design**

The following electrochemical design was used for each cell of the molten-salt secondary battery.

**Electrodes:**

- **Anode:** Magnesium - 6 grams, 0.020-inch thick riveted on Kovar as shown in Figure 25.
- **Cathode:** Nickel - 30 grams, 0.020-inch thick clad on Kovar as shown in Figure 25.

**Electrolyte:**

- **Anolyte:** 150 grams MgCl$_2$, 100 grams NaCl.
- **Catholyte:** 135 grams MgCl$_2$, 90 grams NaCl, 25 grams NiCl$_2$.

The anolyte and catholyte were added to the cell in the solid state. With these materials, a difference in volume occurred between the solid and liquid phases of the eutectics. The cell compartments, therefore, had to be filled partially, then brought to the melting temperature of the eutectic, and allowed to cool and solidify. The remaining salts were then added. This procedure was continued until all of the required electrolyte was introduced. Although time consuming, this method of filling proved to be satisfactory.

3.6.4 **Initial Heat Input vs. Heat Output**

The quantity of heat input necessary to bring the cell described above to operating temperature is calculated below and compared with actual cell output. These calculations are based on an ambient temperature of 25°C.

**Formula:**

\[ Q = W \times c \times \Delta t \]

where:

- **Q** = Heat input (calories)
- **W** = Weight of major materials in cell (grams)
- **c** = Specific heat of major cell materials
- **\Delta t** = Change in temperature from ambient (°C)
<table>
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<th>Specific Heat (°C)</th>
<th>Δt (°C)</th>
<th>Heat Input (calories)</th>
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<tr>
<td>Magnesium</td>
<td>6</td>
<td>.07</td>
<td>525</td>
<td>200</td>
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<tr>
<td>Nickel</td>
<td>30</td>
<td>.10</td>
<td>525</td>
<td>1575</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>500</td>
<td>.20</td>
<td>525</td>
<td>52500</td>
</tr>
<tr>
<td>Alumina Housing</td>
<td>200</td>
<td>.20</td>
<td>525</td>
<td>21000</td>
</tr>
</tbody>
</table>

Total = 75295 calories

Heat Input = 75,295 calories = 87.5 watt-hours
            860 calories/watt-hour

Heat Output = 1.6 volts x 20 amp-hours = 32 watt-hours
Heat Output x 100 percent = \(\frac{32 \times 100}{87.5}\) = 35.4 percent

3.6.5 Heat Loss Due to Cell Radiation

An important factor in the design of a molten salt secondary battery is the calculation of the heat loss of the battery due to cell radiation. Assuming that the sink temperature, \(T_s\), is equal to 0°K, and the operating temperature, \(T_o\), is equal to 550°C or 823°K, then by means of the following formula, the calculation may be made.

**Formula:**

\[ Q = A \alpha \sigma (T_o^h - T_s^h) \]

where:

- \(A\) = outer surface area of cell in square inches
- \(\alpha\) = \(1.1 \times 10^{-12}\) watt/in\(^2\)
- \(\sigma\) = 0.03 emissivity of silver mirror
- \(T_s\) = sink temperature (negligible)
- \(T_o\) = absolute operating temperature in °K.
- \(d\) = diameter (inches)
\[ Q = A \alpha \sigma T^4 \]
\[ A = 2\pi a + \frac{2\pi a^2}{4} \]
\[ A = 2\pi(3.5) \times 2\pi(3.5^2) \]
\[ A = 41 \text{ square inches} \]
\[ Q = 41 \times 1.1 \times 10^{-12} \times (8.23)^4 \times 10^8 \]
\[ Q = 41 \times 1.1 \times 10^{-12} \times 4.6 \times 10^{11} \]
\[ Q = 21 \text{ watts (radiation loss if sink temperature were absolute zero)} \]

The above radiation loss is within 10 percent of the loss that would occur if the sink temperature were at 25°C.
4. CONCLUSIONS AND RECOMMENDATIONS

The present contract has demonstrated the desirable advantages of using the high-capacity anode and cathode materials coupled with a molten-salt electrolyte for the development of new secondary batteries. In order that this concept be further exploited, the following recommendations for future work are presented. A future program should include the three following phases with their respective objectives.

4.1 RESEARCH PHASE

A program is required which will enlarge the scope of the various anode-cathode combinations which were investigated in this study. This will determine the limiting factors in high-current applications. The development of a practical molten-salt secondary battery is dependent upon gaining a thorough understanding of the function of the chemical reactions taking place during charge and discharge conditions.

A fundamental study should be undertaken to determine the effectiveness of a ternary eutectic electrolyte in reducing the operating temperature of a molten-salt secondary battery.

A research program is necessary for the development of a ceramic separator which can replace the mobile sodium ions with mobile lithium or oxygen ions. A lithium-ion permeable ceramic separator is most desirable because it will permit the use of lithium as an anode thereby leading to a lighter weight electrolyte. The lithium-ion separator will also permit rapid diffusion at a relatively low activation level; this can lead to the development of cells capable of operating satisfactorily at a lower temperature.

4.2 DEVELOPMENT PHASE

A detailed characterization is required of the various couple which can be used with molten-salt electrolytes. This is necessary to determine the performance of these cells for use in secondary batteries. The available data are
insufficient to permit making recommendations for its use in application studies. A satisfactory developmental program will include the following areas of endeavor:

   a. increases in the energy-to-weight ratio of the system.
   b. design of efficient power electrodes.
   c. design of a minimum-weight, minimum-volume battery package which can achieve the desired operating life requirements.
   d. establishment of techniques to obtain and maintain the desired operating temperature.
   e. establishment of parameters such as power density, energy efficiency, and charge retention.

4.3 SERVICE TEST

A service-test program is necessary to evaluate molten-salt secondary batteries for selected applications. This program will provide detailed information on their performance in the field, and should be initiated as soon as sufficient data from the above development phase are available.
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