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DIMINIODE THERMIonic ENERGY CONVERSION
WITH LANTHANUM-HEXABORIDE ELECTRODES

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ABSTRACT

This paper presents thermionic-conversion data obtained from a variable-gap cesium diminiode with a hot-pressed, sintered lanthanum-hexaboride emitter and an arc-melted lanthanum-hexaboride collector. Performance curves cover a range of temperatures: emitter 1500 to 1700 K, collector 750 to 1000 K, and cesium reservoir 370 to 510 K. Calculated values of emitter and collector work functions and barrier index are also given.

INTRODUCTION

TEC with metal-hexaboride electrodes (ref. 1) was part of a diode-screening project at the Lewis Research Center (LeRC) in 1970. The work depended on economical "mass production" of the diminiode, shown in figure 1 (refs. 2 to 5). This cesium diode had been designed with guarded electrodes small enough to accommodate obtainable 0.04-cm-diameter single crystals of refractory materials like tungsten, rhenium, iridium (ref. 6), and metal hexaborides. In fact procurement initiated in February 1971 for 0.8-cm-diameter LaB$_6$ single crystals to be made by R. W. Johnson (ref. 7). But the in-core nuclear thermionic program incorporated the diminiode capability for a statistical study of reactor-compatible electrode materials (refs. 8 to 10). During the 1973 termination of space nuclear activities (including TEC) an attempt to evaluate a diminiode with LaB$_6$ electrodes fell short. Subsequently presentation at the 1974 IEEE International Conference on Plasma Science reviewed TEC electrodes of LaB$_6$ and other metallides (ref. 1) in conjunction with the diminiode (ref. 11). Then the current work began with LeRC's technical and fiscal management of NASA's applied-research-and-technology (ART) program for TEC in July 1975 (refs. 12 to 17).

NASA's TEC-ART Program prompted important new information on metal hexaborides and LaB$_6$ in particular (refs. 18 to 26). Additional emphasis came
with the July 1977 revelation of 1.7-V barrier indices for cesium diodes with LaB$_6$ collectors at the Sukhumi Institute of Physics and Technology (ref. 27). Shortly thereafter programmatic retrenchment terminated TEC-ART activities at LeRC. And NASA transferred fiscal and technical management of its TEC-ART program to the Jet Propulsion Laboratory (JPL), where NEP-prototype emphasis (refs. 28 to 34) has led to indicated discontinuations of research on metal hexaborides.

In the interim LeRC overcame impurity and attachment problems for LaB$_6$ electrodes in a diode with a hot-press-sintered emitter and an arc-melted collector. And after a long source search 0.8-cm-diameter single crystals are on order for LaB$_6$ and are available for the even more promising cerium hexaboride (CeB$_6$). Diminioide evaluations of the better-performing metal-hexaboride crystal faces would allow optimum-surface selections. Then parametrically contro11ed vapor deposition should enable an approach to such desirable TEC-electrode surfaces in practical cylindric configurations. But diminioide personnel and facilities will be dispersed before the monocrystalline metal hexaborides arrive.

Fortunately some preliminary results for the diode with 99.8 percent-pure LaB$_6$ electrodes are now available. These data represent a 1500 to 1700 K sintered LaB$_6$ emitter, a 750 to 1000 K arc-melted LaB$_6$ collector, a 370 to 510 K cesium reservoir, and 0.25 mm interelectrode spacing. The present paper discusses performance values obtained from this thermionic energy converter with emitter and collector surfaces of LaB$_6$.

W. E. Frey and R. D. Schaal developed and performed special procedures and conducted research tests necessary to fabricate this diminishoide. References 4, 5, and 10 provide detailed descriptions of all equipment and procedures used in the experiments treated in this paper.

ELECTRODE MATERIAL PROCESSING

Many types of lanthanum hexaboride (LaB$_6$) were purchased or formed in-house in an attempt to fabricate thermionic diode electrodes. These forms of LaB$_6$ powder were tried: cold-pressed; hot-pressed; electron-beam melted; arc-melted; and hot-pressed, sintered as well as single crystal. Some of the problems encountered were high impurity levels, low material strengths, high porosities, voids, cracks, small sample sizes, various reactivities, and thermal expansion mismatches. The best form for a diode would be of course a 0.7-cm-diameter, high-purity, oriented, uniform, single crystal of LaB$_6$. Since this form was not available the following polycrystalline LaB$_6$ material was used.
The collector electrode started with hot pressed 85 percent dense and 99.8 percent pure LaB₆. This hot-pressed material was arc melted into a high-density button. The button was shaped by an electrical-discharge machine (EDM) into a 0.780-cm-diameter by 0.185-cm-thick disk for the collector. A Zr, 22.8 w/o-Ru braze (1523 K melt point) was used to attach the collector to a diminiode niobium, alumina-cermet sub-assembly. The final preparation of the collector face and guard ring separation was done by EDMing. A heat-cycle test was performed on this collector sub-assembly in an RF vacuum furnace. The sub-assembly was heated 10 times from room temperature to 1073 K at <10⁻⁶ torr.

The biggest problem with the LaB₆ emitter electrode was finding a method to attach it to the diminiode tantalum-top-hat structure. Many brazing or adhesive materials were tried to adhere LaB₆ to Ta for high-temperature emitter applications. References 1 and 39 mention most of the materials tried. Failure was more common than not for several reasons. The major cause of failure was a high reactivity of LaB₆ at temperatures above 1500 K with practically all materials tried. Another reason was the brittleness of LaB₆ which caused cracking under the stress, generally as a result of thermal cycling and thermal expansion mismatch. Additionally, some materials, such as Pt and MoSi₂, wicked into the porous LaB₆ and contaminated the electrode surface.

Special low vapor pressure (<10⁻¹⁰ torr at 1500 K) braze alloys were prepared and used with LaB₆ (ref. 40). The alloy Zr, 22.8 w/o-Ru which melts at about 1523 K was a fair braze but applicable only for the low temperature collector electrode. A Zr, 31.1 w/o-Mo braze was fair as an emitter braze but limited to about 1700 K maximum due to reactions and remelting problems.

Attempts were made to melt LaB₆ on W, Ta, and Mo pedestals. Generally, a reaction occurs well before the melting of LaB₆, thereby raising doubts as to the chemical integrity of an electrode joined by this method. Further proof of chemical diffusion was the depression of the LaB₆ melting point by 200 to 400 K below literature values.

Clean metal-to-metal diffusion bonding also had the problem of LaB₆ reactions. As a result, TaC coated Ta was tried as the base pedestal. Limited success occurred in that reactions were prevented. The bonding, in general, did not hold up after thermal cycling to about 1700 K. Subsequently, private communications with E. K. Storms (LASL) indicated 150 cycles to over 1772 K without failure for a TaCo₂ braze of LaB₆.

At this point it was concluded that a more readily attainable method to hold the LaB₆ would be mostly mechanical. A tantalum carbide coating was used to prevent LaB₆ from reacting with a tantalum cup into which it was hot-press
sintered. Several different configurations were tried. The one that worked best is described below.

A carbonized tantalum cup as shown in figure 2 was machined. The carbonizing was accomplished by packing carbon powder into the tantalum cup and RF heating in a vacuum for 1 hour at 2100 K. The excess carbon powder was removed from the cup and 320-mesh, high-purity LaB₆ powder was cold pressed into the cup. The tantalum cup and LaB₆ were RF heated to 2100 K for 2 hours in a vacuum with a tantalum rod pushing on the LaB₆ with a constant 210 N/cm² (305 psi) pressure to sinter the LaB₆.

Since the LaB₆ was below the tantalum cup surface, the excess tantalum was removed using high speed tools. No EDMing was done on this electrode because of past experience which showed a loosening of the sintered LaB₆ material in the tantalum cup after EDMing. The surface of the LaB₆ emitter was prepared using fine emery paper. A Zr, 18 w/o-Re braze alloy (melting point 1870 K) was used to bond the Ta₆ LaB₆ cup to the tantalum top hat of the diminiode. This sub-assembly was heated at <10⁻⁶ torr for 10 cycles from room temperature to 1700 K. The bond between the LaB₆ and tantalum remained good as was observed from the constant temperature difference at a given temperature between the LaB₆ and tantalum.

One additional property measured on the sintered LaB₆ was its thermal expansion. As can be seen in figure 3, the thermal expansion of sintered LaB₆ matches that of annealed niobium (ref. 30). This means that the diminiode collector sub-assembly has a good thermal expansion match. The emitter sub-assembly has the LaB₆ in compression which should make a good mechanical bond.

After any parts of the diminiode were subjected to cutting fluids or contamination of any kind, they were ultrasonically cleaned in trichloroethane (NA 500) before vacuum bakeout, welding, brazing, or assembly.

At this point the two basic electrode sub-assemblies were ready for final assembly. For a detailed description of the diminiode assembly, see reference 11 (note that the cesium fill procedure, given below, has been modified so that capsules are no longer used).

**DIMINIODE PROCESSING**

A new processing chamber was used for the LaB₆ diminiode. This chamber shown in figure 4 allows diminiode bake-out, emitter-top-hat-temperature calibration, electrode-spacing calibrations, cesium filling and a copper-braze
closure. Both turbomolecular and vac-ion pumping are used on this water-jacketed chamber to maintain $10^{-8}$ torr (diminiode cold) and $10^{-7}$ torr (diminiode hot).

In this case the LaB$_6$ diminiode was electron-bombardment (EB) heated to 1673 K emitter and a 933 K collector temperature for bakeout. A temperature calibration of the black-body hole in the LaB$_6$ (sighting down the open cesium-reservoir tube) versus the black-body hole in the top hat was done. As indicated in references 37 and 38, this calibration is acceptable because the diminiode holds at zero current before and after the data-taking cycle. These low-transport conditions and thermal inertia assure good sensing of the emitter temperature. The electrode gap was also checked at this time with the diminiode hot.

Cesium is introduced into the chamber from a high-purity cesium bottle through a heated stainless-steel tube as shown in figure 5. The flow is controlled with a metal seal stainless-steel valve. The cesium is dropped from the end of the tube onto a small, heated stainless steel tray. After visually observing the cesium, the tray can be tipped to allow the cesium to run into the diminiode or into a catch can. Following cesium addition a tantalum ball is then dropped into the end of the cesium reservoir and copper brazed in place to seal the diminiode.

The diminiode is now ready for performance testing after it is removed from the processing chamber and mounted into the test station.

**DIMINIODE RESULTS**

Figure 6 shows the current-density, voltage ($I$, $V$) envelopes for constant emitter temperatures of 1500, 1550, 1600, 1650, and 1700 K with the collector varied from 750 to 1000 K and the cesium reservoir varied over a temperature range of 510 to 370 K. The power density ($P$, $V$) envelopes calculated from the $I$, $V$ results are shown in figure 7. These two figures are summarized in the following table to show where maximum power occurred.
<table>
<thead>
<tr>
<th>Emitter temperature, $T_E$, K</th>
<th>Approximate collector temperature, $T_c'$, K</th>
<th>Approximate cesium temperature, K</th>
<th>Maximum power output, $P_{max}$ W/cm²</th>
<th>Voltage at maximum power, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>850</td>
<td>440</td>
<td>1.86</td>
<td>0.22</td>
</tr>
<tr>
<td>1550</td>
<td>850</td>
<td>440</td>
<td>2.50</td>
<td>0.28</td>
</tr>
<tr>
<td>1600</td>
<td>850</td>
<td>440</td>
<td>3.50</td>
<td>0.38</td>
</tr>
<tr>
<td>1650</td>
<td>850</td>
<td>450</td>
<td>4.20</td>
<td>0.40</td>
</tr>
<tr>
<td>1700</td>
<td>900</td>
<td>460</td>
<td>5.29</td>
<td>0.45</td>
</tr>
</tbody>
</table>

As can be seen from the table, the cesium reservoir temperatures are much lower than the expected 550 K. Cesium reservoir thermocouples and readout instrumentation were checked with no apparent discrepancies found. A procedure check revealed that more cesium was added to this dimiinode than was usual. Steps taken to ascertain possible cesium temperature problems are described below.

The dimiinode was carefully removed and X-rays were taken to see if any cesium extended beyond the cesium-temperature control zone. The reservoir tube axis is in a 3° below horizontal position during operation. No apparent cesium extension could be seen.

The dimiinode was then positioned with the cesium-reservoir pointing down. The reservoir was cooled and the rest of the dimiinode heated with an air heat gun to make sure all the cesium was in the reservoir. Another set of X-rays was taken. No cesium could be seen above the cesium-reservoir-temperature control zone.

The dimiinode was then placed in its normal operating position. Hot water was used to heat the cesium reservoir with the rest of the dimiinode at room temperature. After heating in this manner for 5 to 10 minutes the reservoir was cooled and another series of X-rays taken. This time the X-rays revealed cesium in the unheated portion of the cesium reservoir tube. At this point the decision was made to remount the dimiinode in its test station with the cesium reservoir pointing down to prevent any possible cesium extension beyond the control zone.

When trying to test the dimiinode in this new position it was discovered that the collector was no longer operative. Apparently a large segment of the collector had dislodged locally, but not enough to short out another element. Arc-melted samples had demonstrated this separating tendency. A series of
runs was made using the guard ring as the collector to see if there were any
changes in the cesium reservoir temperature for maximum power. Maximum
power occurred at a cesium reservoir temperature of 450 to 460 K at 1500 K
emitter and 850 K collector temperatures. Thus the dimode apparently did
operate at the cesium-reservoir temperatures indicated with a possible error
of ±25°.

A comparison of the I, V and P, V envelopes of the LaB₆ dimode with a
TECO W, O, Cs diode, and a Re, Nb diode all with 1700 K emitters is shown
in figure 8. As can be seen in this figure the LaB₆ dimode produces a maxi-

mum power that is almost equal to the best diode (Re, Nb) but at almost twice
the voltage, 0.45 volt versus 0.23 volt.

Indeed the most efficient operation of the LaB₆ dimode occurs at 0.75
volt and 5 A/cm² (3.8 W/cm²). There the work function of the 1700 K emitter
is less than 2.64 eV, the barrier index is about 1.9 volts, and the calculated
efficiency for optimum leads is approximately 1.1 percent. Unfortunately back
emission data to enable determination of the work function for the 853 K col-
lector was unavailable.

In fact because of the complete lack of experience with cesium diodes
having LaB₆ emitters and collectors, these initial tests were made based on
accumulated results for refractory-metal electrodes. As such these findings
are very nonoptimum. And a search of the data collection revealed no suitable
back-emission numbers. Correcting this deficiency was a goal of the next set
of tests before changing the interelectrode spacing. But the collector malfunc-
tion intervened.

Additional I, V curves did reveal barrier indices less than 1.95 volts for
both 1053 and 1596 K emitters: 1053 K emitter, 801 K collector, 0.02 V,
4.8 A/cm², 3.0 W/cm², <2.57 eV emitter work function, ~1.95 V barrier
index and 1596 K emitter, 853 K collector, 5.3 A/cm², 0.51 V, 2.7 W/cm²,
<2.46 emitter work function, ~1.95 V barrier index.

CONCLUDING REMARKS

As can be seen in the dimode results, the performance of the LaB₆ is
equal to some of the best electrode combinations at this time. It is felt that
the LaB₆ material and electrode spacing used in this test are far from the
optimum. Work functions for single crystal LaB₆ are \( \varphi_{LaB₆(100)} = 2.52 \) eV,
\( \varphi_{LaB₆(110)} = 2.60 \) eV, and \( \varphi_{LaB₆(346)} = 2.41 \) eV.
Field emission work by L. Swanson indicates even lower work functions are available. Swanson also obtained nonoptimized cesiated LaB$_6$(100) work functions of 1.3 eV (refs. 17 to 21) without oxygenation. With collector work functions approaching this low value and interelectrode losses diminished by reduced cesium pressures perhaps coupled with some enhancement, barrier indices significantly lower than the measured 1.9 eV value seem quite probable. Furthermore the work function for CeB$_6$(100) is less than LaB$_6$(100), which is even more promising.

Incidentally reference 41 indicates vaporization rates between $4 \times 10^{-3}$ (LaB$_6$,014) and $4 \times 10^{-4}$ (LaB$_6$,114) cm/yr (2 to 0.2 mils/yr) for congruently vaporizing LaB$_6$ at 1700 K. So TEC with 1700 K congruently vaporizing LaB$_6$ emitter surfaces and congruently depositing LaB$_6$ collector surfaces appear practical both in performance and lifetime. The interelectrode gap would merely shift between 0.04 and 0.004 cm (16 and 2 mils) in 10 years of service.

Work with promising metallides like LaB$_6$ and CeB$_6$ for TEC electrodes should include tests of selected faces (refs. 17 to 21) of high-purity single crystals of specified stoichiometries (refs. 17 to 23). If such systematic research is neglected, a far more complex situation could result than occurred for refractory-metal TEC electrodes in the early 1960's. Understanding and control of TEC variables had eluded researchers for many years. Finally investigations of pure, oriented monocrystalline electrodes in exceedingly clean converters lifted the veil to reveal a systematic technology where confusion formerly prevailed. Having defined and described the datum base for refractory-metal electrodes, TEC research workers could then invoke crystal-face and additive effects predictably - rather than haphazardly.

Metallide TEC electrodes begin with more chemical complexity, hence greater permutability than the relatively simple single elements of their refractory-metal counterparts. Thus systematic research to point the way to controlled, productive development is even more important for success with metallide TEC electrodes than it ultimately proved to be for the refractory-metal predecessors.
REFERENCES


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THREE "C" CLAMPS USED WITH PRECISION SHIMS FOR SPACING

(a) DIMINIODE CROSS SECTION.

(b) DIMINIODE MOUNTED ON FLANGE.

Figure 1. - Diminiode.
Figure 2. - Tantalum cup for sintering LaB$_6$ emitter.

Figure 3. - Thermal expansion (ref. 35).
Figure 4. - Processing chamber parts.

Figure 5. - Processing chamber schematic.
Figure 6. - LaB₆, LaB₆ constant emitter temperature envelopes, optimum collector and reservoir. 0.25 mm gap.

Figure 7. - LaB₆, LaB₆ constant emitter temperature envelopes, optimum collector and reservoirs.
Figure 8. - Constant emitter temperature envelopes
1700 K emitter, optimum collector and reservoir.
0.25 mm gap.